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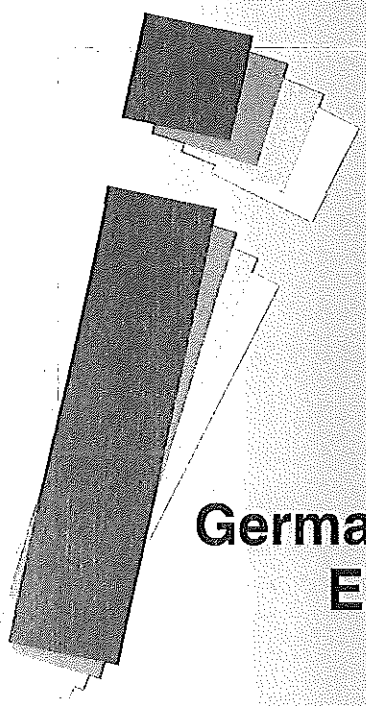

German-Egyptian Seminar on Environmental Research

Cairo
March 21 – 23, 1994

edited by
H.F. Aly
D. Nentwich

Forschungszentrum Jülich GmbH
Bilateral Seminars of the International Bureau

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German-Egyptian Seminar

on

Environmental Research

Cairo, March 21 to 23, 1994

Monday, 21.03.1994

09:00 h Opening Ceremony and Overview Lectures

10:00 h Break

Atmospheric Research

10:30 h Photochemical Reactions of Pollutants in the Troposhere
H. Güsten

11:30 h Ozone Formation in the Greater Cairo Area
G. Heinrich

12:00 h Construction of an emperical relation for surface ozone over Greater Cairo
A.B. Ramadan

12:30 h Ozone in the Western Desert of Egypt
D. Sprung

13:00 h Lunch

Waste Reduction

14:00 h The LAWI plant: An instrument for waste reduction with minimized environmental impact
W. Krug

15:00 h First Results in the incineration of burnable simulated municipal solid waste
A.Z. Ahmed

15:30 h Treatment of industrial waste effluents by pyrolysis residue
A.A.M. Daifullah

Tuesday, 22.03.1994

Toxic Metals in the Biosphere

09:00 h Uptake of heavy metals by crops
H. Helal

10:00 h Analytical methods used in determining trace elements
R. Garten

11:00 h Break

11:30 h Trace metal pollutants in El Manzala lakes by inductively coupled plasma spectroscopy
S. El Alfy

12:30 h Assessment of pollutants in Lake Manzala using gamma-ray spectroscopy
R. Zaghloul

13:00 h Lunch

Environmental Specimen Banking

14:00 h The environmental specimen bank in the Federal Republic of Germany
M. Schwuger

14:45 h Inorganic analysis within the German environmental specimen bank
H. Emons

15:30 h Organic analysis within the German environmental specimen bank
J.D. Schladot

16:15 h Comparative Analysis of water and sediments from fresh water compartments in Egypt and Germany
S. Shawky

Wednesday, 23.03.1994

Agricultural Research (Parallel Session)

09:00 h Low input concept for desert agriculture
H. Helal

10:00 h Use of N-15 for better fertilizer management under desert environment
A. Monem

10:45 h Break

11:00 h Benefits of Organic Matter (Humus) in Arid Irrigated Soils
K. Haider

Appropriate Architecture

11:15 h Environment - a challenge for architecture
L. Christians

12:15 h Energy saving building materials and construction technologies for tropical climates
G. Minke

13:00 h New Approach for Desert Development
S. Algohary

13:30 h Lunch

Radioisotopes in the Biosphere (Parallel Session)

09:00 h Determination of radioisotopes in environmental samples
M. Pimpl

09:30 h Measurement of Radioactivity levels in soil in the Nile Delta and Middle Egypt
N.M. Ibrahiem

09:45 h Uranium concentrations in sediments for the Suez Canal
N.M. Ibrahiem

10:00 h Determination of Radon and Radon Daughters in Air
E. Piesch

10:30 h Seasonal Variation of Radon Concentration in Egyptian Dwellings
G. Hassib

11:00 h Break

P R E F A C E

The formalized links in scientific cooperation between the Federal Republic of Germany and the Arab Republic of Egypt have become tradition. The oldest agreement in this respect is the Governmental Agreement on Cooperation in Scientific Research and Technological Development signed on 11.4.1979, which was later followed by the Agreement on Cooperation in the Peaceful Use of Nuclear Energy, signed on 26.10.1981.

These Agreements provide the political and legal embedding for those research entities in both countries which wish to embark on joint cooperation ventures. The Atomic Energy Authority on the Egyptian side and the Forschungszentrum Jülich GmbH (KFA) have been designated by their respective Governments to implement cooperative ventures, for which purpose they have signed a Special Arrangement on 17.2.1983. This Arrangement is the basis for a multitude of joint research activities which have been implemented with outstanding success over the past years and which will continue to provide the frame for future ventures to come.

Undoubtedly, nuclear energy research was in the mainstream of interest in both countries when this formalized cooperation between KFA and AEA started. In the meantime, industrial development and scientific advancement have opened new frontiers of interest and challenges. Anthropogenic activities are increasingly upsetting the natural environmental balance and are at the same time shifting from local impact to global importance. Science is confronted with the challenge to answer the question of what are the consequences of anthropogenic changes to the environment and to help politics formulate countermeasures for the sake of a sustainable future. AEA and KFA have jointly taken up part of this challenge and have embarked on a series of joint projects such as Atmospheric Research, Waste Reduction Techniques, Toxic Metals and Radioisotopes in the Biosphere, Environmental Specimen Banking, Agricultural Research and Appropriate Architecture.

These proceedings contain the lectures presented at the first German-Egyptian Seminar on Environmental Research held in Cairo from March 21 to 23, 1994. The aim of the seminar was twofold. First, project results achieved within the Egyptian-German cooperation where presented to the scientific community and to the interested public and discussions on future lines of actions took place. Secondly, the seminar was also organized in appreciation of the merits of the resigning chairman of AEA, Prof. Dr. Fawzy Hammad, who has been instrumental in shifting the main R&D activities of AEA and of the Egyptian-German cooperation into the environmental area, whereby the know-how and the techniques accumulated and developed in former times in areas related to nuclear energy research where transferred to this modern field of science. Due to his forsight, the basis is given for the generation of young scientists coming into responsibility to contribute their share to the solving of the worlds global challenges.

The Editors

PHOTOCHEMICAL REACTIONS OF POLLUTANTS IN THE TROPOSPHERE

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Abstract

An introduction to the present knowledge of chemistry of the reactions involved in photochemical air pollution is given with special emphasis on the situation in urban areas. The general mechanisms are described for the generation of oxidising radicals in the troposphere which are responsible for the chemical oxidation and degradation of atmospheric pollutants.

Introduction

Air pollution was originally regarded as a sign of industrial activity and economic progress. However, the exponentially growing population and industrialising society have caused serious air pollution problems on a local and a global scale during the second half of the twentieth century.

Among the primary pollutants (SO_2, NO, NO_2, CO, CO_2, CH_4 and hydrocarbons) in the gaseous phase, sulfur and nitrogen compounds exceed in their source strength already the natural emissions. Anthropogenic sources are in general transportation, stationary fuel combustions, industrial processes, waste disposal and incineration. Recently, also new natural sources have been identified which, however, are related with the food production for more than 5 billion (10^9) people, e.g. CH_4 from cattle and rice paddies, N_2O from fertilizers. Beyond the gaseous emissions considerable amounts of particles and dusts are transported in the troposphere. Current estimates of the magnitude of anthropogenic emissions of atmospheric aerosols are very uncertain and range between 5 - 30 % of the natural production. It seems that the source strength of soil-generated aerosols exceeds the amount of aerosols injected into the atmosphere by volcanoes, forest wildfires and meteorites. The total Sahara dust transported via the four cardinal points amounts to 750 - 800 Mt/year. It is conceivable that an enhanced photocatalytic degradation or oxidation of atmospheric pollutants can occur on the surface of the atmospheric aerosols (Güsten, 1986a).

Generation of free radicals in the troposphere

Chemical reactions of gaseous air pollutants in the troposphere are described in terms of chemical kinetics, i.e. the rate of degradation is given as a rate constant k_1,

$$\frac{dS}{dt} = k_1 \cdot [R] \qquad [1]$$

for the chemical reaction of pollutants S with an existing radical R. Since concentrations of the oxidising radicals in the free troposphere are about a factor of 10^3 smaller than the concentration of the atmospheric pollutants, reaction [1] is considered as pseudo-first order reaction. The main oxidising radical in the troposphere is the OH radical. It is generated via the photolysis of ozone with UV light below 315 nm (Fig. 1):

$$O_3 + h\nu\,(< 315\,\text{nm}) \rightarrow\ O_2 + O\,(^1D). \qquad (1)$$

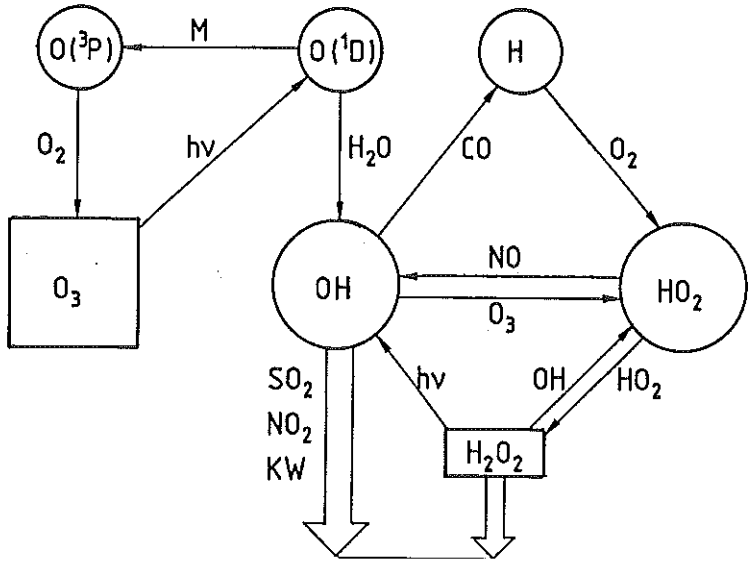

Fig. 1: Reaction scheme of the generation of free radicals in the troposphere.

The electronically excited oxygen atom (O^1D) reacts with water vapour to form the OH radical:

$$O\,(^1D) + H_2O \rightarrow 2\,OH.$$

The average lifetime of the OH radical in the troposphere is approximately 1 second. The general reaction of the OH radical with an air pollutant is

$$RH + OH \rightarrow R + H_2O \qquad (2)$$

$$R + O_2 \rightarrow R{-}O{-}O. \qquad (3)$$

Dimerisation of two HO_2 radicals yield H_2O_2, a powerful oxidising secondary air pollutant (Zellner, 1986).

Most organic and inorganic atmospheric pollutants are oxidised by OH radicals in the troposphere. Thus, the OH radical plays a key role in the degradation of atmospheric

pollutants. The rate of reaction of the OH radical with an air pollutant in the gas-phase often determines the upper limit of the tropospheric lifetime and, hence, the persistence of an organic molecule in the troposphere. The only class of organic compounds of which is known that they do not react with OH radicals is the fully halogenated alkanes (chlorofluorohydrocarbons). The tropospheric half-life $\tau_{1/2}$, can be calculated by assuming a pseudo-first order behaviour:

$$\tau_{1/2} = \frac{ln2}{k_{OH}[OH]} \quad [2]$$

The average global tropospheric OH concentration is approximately 5 x 10^5 OH radicals per cm^3. The OH radical is considered as the "vacuum cleaner" of the troposphere; it determines the amount of anthropogenic pollutants which is transported to the stratosphere (Güsten et al., 1984).

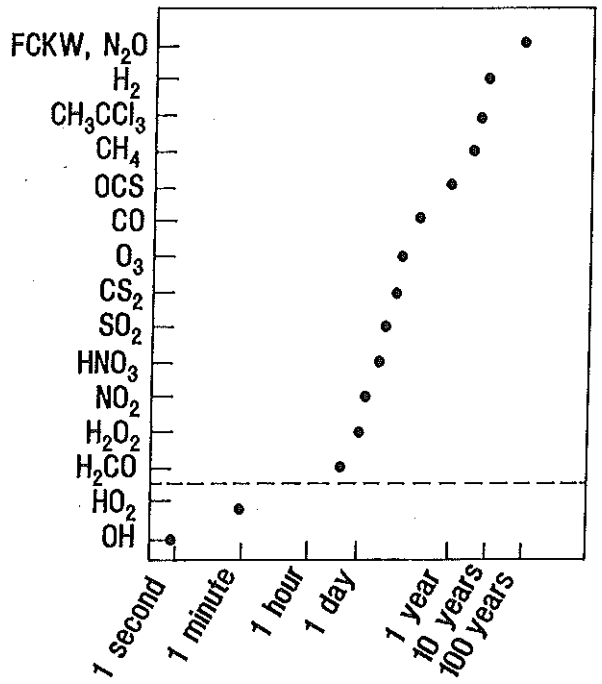

Fig 2: Tropospheric lifetime of natural and anthropogenic trace gases.

Generally, the lifetime of trace gases range from hours to many years (Fig. 2). Above a tropospheric lifetime of 10 years air pollutants can slowly diffuse into the stratosphere (Chlorofluorohydrocarbons etc.).

Chemical reactions in the troposphere

Acid rain

Acid rain is the final product of the atmospheric oxidation of SO_2 and NO_x (NO + NO_2). Major products are sulfuric and nitric acid as well as their salts (Calvert and Stockwell, 1983).

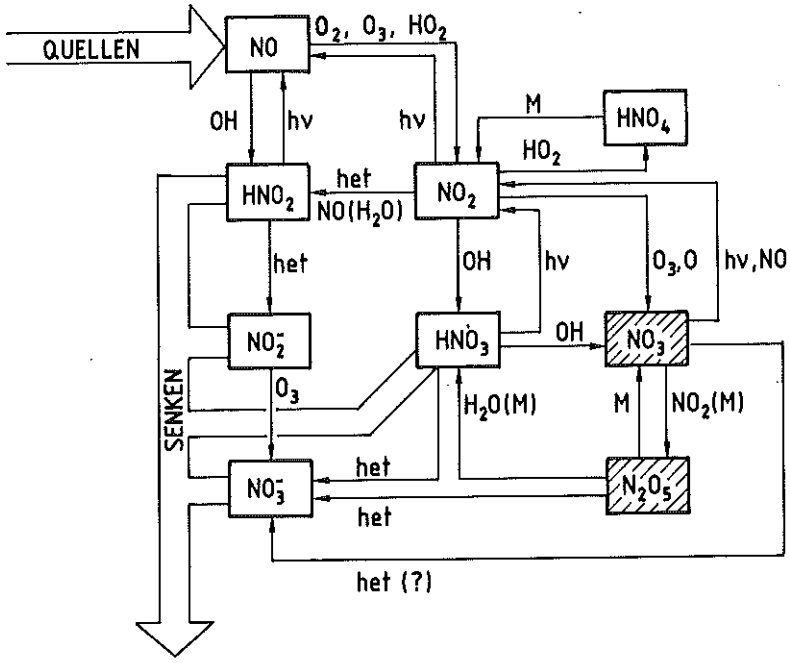

Fig. 3: Reaction scheme of the atmospheric oxidation of NO_x (het = heterogeneous reactions; hatched = present only in the night).

The gas-phase oxidation of SO_2 is fairly slow, a few per cent per hour, equivalent to a tropospheric life-time of one week. Thus, SO_2 and their oxidation products can be transported over thousands of kilometers. Since SO_2 is quite soluble in water the oxidation of SO_2 in clouds can be very effective. It has been shown that H_2O_2 rapidly oxidises SO_2 in fog and clouds. It is believed that oxidation of SO_2 in the wet-phase gives rise to the acid rain, much more than the contribution through oxidation in the gas-phase.

The global emissions of NO_x from anthropogenic sources exceed in the meantime those from natural sources. The stable end product of their oxidation are HNO_3 and to a minor extent HNO_2 (~10 %) or their salts (Fig. 3).

The OH radical reacts rapidly with NO or NO_2, approximately 10 times faster than with SO_2, to yield HNO_2 and HNO_3. Thus, acid rain is composed by HNO_3 (HNO_2) and H_2SO_4. Depending on the availability of bases like NH_3 in the air, the major fraction can well be

ammonium sulfat etc. Depending on the transport distance, acid rain relatively near to the source, contains more HNO_3 while at longer distances the relative amount of H_2SO_4 increases. Since these compounds are photochemically stable and highly soluble in water their final fate is wet or dry deposition to the Earth's surface.

Photochemical smog

Photochemical smog is the result of photochemical reactions of primary pollutants (NO_x and hydrocarbons) converted by sunlight in the wavelength of 300 - 400 mm to secondary pollutants, like ozone, aldehydes, ketones, PAN etc. All the reaction products of photochemical smog formation are termed photo-oxidants. Ozone is the main reaction product and thus an indicator of the general level of photo-oxidants. The formation of photochemical smog can be simulated in so-called smog chambers by irradiating an reactive olefine (Leighton, 1961; Demerjian et al., 1974; Güsten, 1986b).

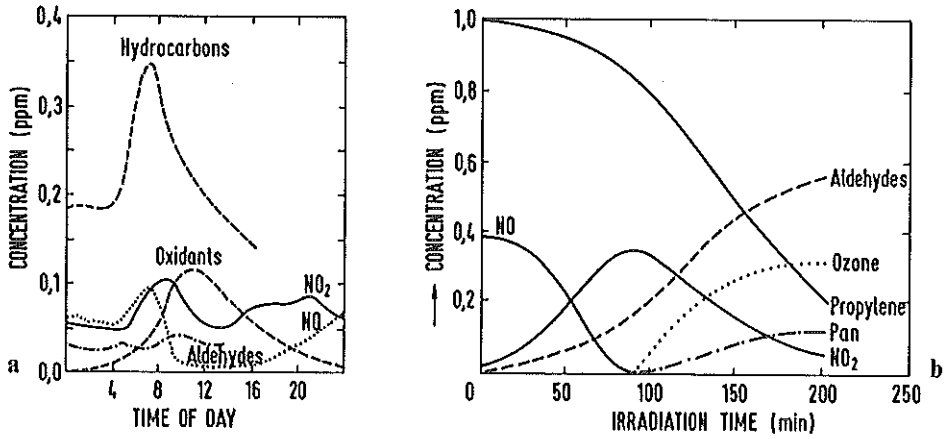

Fig. 4: The diurnal variation of photochemical smog buildup in Los Angeles (a) and the concentration-time profiles of various compounds in a UV irradiated mixture of nitric oxide and propylene in air (b).

In Fig. 4 the diurnal variation of the concentration of the oxides of nitrogen and ozone on a smoggy day in Los Angeles are juxtaposed to the time history of the photochemical reaction of a dilute olefine or automobile exhaust with light in the wavelength range of 300 - 420 nm in a smog chamber. In general, the following events take place:

- Nitric oxide (NO) is converted to nitrogen dioxide (NO_2).
- When all of the NO has disappeared, ozone starts to appear.
- The hydrocarbons are oxidised and disappear.
- Other reaction products such as aldehydes and PAN are formed.

The products of photochemical smog above a certain concentration (~60 -80 ppb) lead to

- eye irritation, discomfort and fatigue,
- damage to vegetation, production loss in crops,
- damage to organic material (rubber, paint, organic tissue).

A general scheme for the formation of photochemical smog is depicted in Fig. 5. Besides rapid reactions of NO, NO_2 and ozone to an equilibrium, as indicated on the left side of the scheme, additional ozone is formed on the right side in complicated chain reactions driven by free radicals regenerating NO_2 from NO. In particular, the chain reactions are responsible for the rapid conversion of the unburned hydrocarbons to photo-oxidants within a few hours above an urban area (Güsten, 1986b).

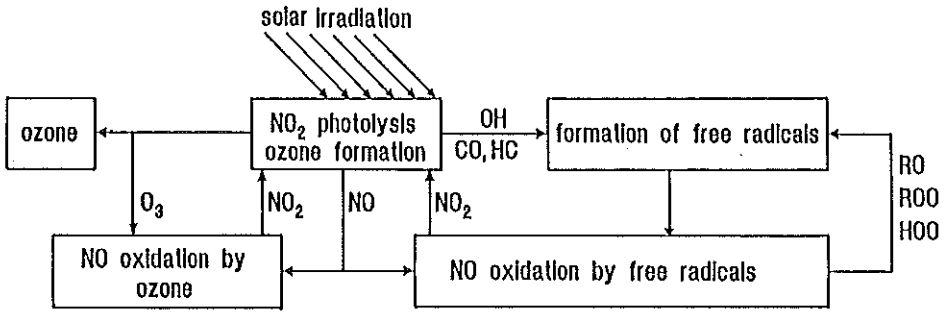

Fig. 5: Scheme of the formation of photochemical smog.

The formation of photochemical smog is started through the photolysis of NO_2:

$$NO_2 + \text{light}\ (\lambda < 400\ \text{mm}) \rightarrow NO + O \qquad (4)$$

$$O + O_2 + M \rightarrow O_3 + M. \qquad (5)$$

A fraction of the NO emitted in the air parcel reacts with ozone to generate NO_2:

$$O_3 + NO \leftrightarrows NO_2 + O_2. \qquad (6)$$

Since Eq. 6 proceeds very rapidly, a photostationary state between NO, NO_2 and ozone is set up. The quasi-steady state in Eq. 6 is only valid at day time since it is driven by sunlight. Free radicals in the complex reactions such as OH, HO_2 and alkylperoxy (RO_2) are the dominant species which are the chain carriers in the additonal NO to NO_2 conversion:

$$\text{Hydrocarbon} + OH + O_2 \rightarrow \text{Products} + HO_2 + O_2 \qquad (7)$$

$$HO_2\,(RO_2) + NO \rightarrow OH\,(RO) + NO_2. \qquad (8)$$

In these catalytic cycles (see Fig. 5) the free radicals contribute very effectively in the additional formation of ozone. Thus, the final concentration of ozone in photochemical smog is very much determined by the concentration of its precursors, namely NO_x and unburned hydrocarbons. Thus, in a city like Cairo, on sunny days at noon time several 100 tons of ozone have been formed from its precursors NO_x and hydrocarbons.

In urban areas ground-level ozone is frequently used as an indicator of photochemical smog (Demerjian et al., 1974; Güsten, 1986b). According to Singh et al. (1978) typical ozone concentrations in clean remote atmospheres range from 20 - 40 ppb. Thus, concentrations of ozone - an indicator of photochemical smog - above 40 ppb are undoubtedly "anthropogenic" or man-made ozone levels. There is growing evidence that tropospheric ozone over populated areas of Europe and North America has doubled during the last century and is currently increasing at an annual rate of about 1 % (Logan, 1985).

In the following lectures of this Symposium reports will be given on the ozone formation potential of the Greater Cairo Area and on the ozone concentrations measured in the Western Desert of Egypt. It is interesting to note that as early as 1874 ozone was measured in the Egyptian desert (Zittel, 1874).

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OZONE FORMATION IN THE GREATER CAIRO AREA

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Abstract

Ozone formation in the Greater Cairo area was studied in 1990 in a three weeks measurement campaign performed at three sites (Shoubra El-Kheima, Mokattam Hill, Helwan) covering a north-south direction of 27 km, and in 1991, from the beginning of April until the end of October, by measurement of the seasonal variation of ozone at one site at El-Kobba. The sinusoidal shape in the diurnal volume fraction plots with peak values of 120 ppb and daily mean value of 50 ppb throughout the year indicate a substantial contribution of photochemistry to the ozone content of the atmosphere. Ozone is produced predominantly over the industrial area in the north and in the centre of Cairo and transported southward by the prevailing northerly winds. Contrary to many urban areas in Europe and in North America, fairly high average ozone levels of 40 ppb are observed during the night throughout the spring and the summer. This may imply that health hazards and crop damage are higher in the Greater Cairo area than in Central Europe.

Introduction

Ozone measurements in the Mediterranean region [1], above all in Greece [2, 3], make evident serious problems of photochemical air pollution in those areas having more sunny days per year than Central Europe. Under a German-Egyptian project of scientific cooperation ozone levels in Greater Cairo were measured. The Greater Cairo area encompasses 27 % (about 13 milllion) of the Egyptian population, 64 % of the industry and 45 % (about 1 million in 1991) of the motor vehicles in Egypt. Low energy prices have encouraged the rapid growth of industry and wasteful use of energy. The number of vehicles increased by 10 % per annum and the electricity consumption by 8.7 % per annum during the decade from 1980 to 1990. Thus, Greater Cairo, already one of the largest cities of the world, is expected to attain a number of almost 20 million by the year 2000. It is clear from these statistics that the population of Greater Cairo is exposed to an alarming level of air pollution. Owing to these facts and its location at the latitude 30° N with more

than 340 days per year of sunshine it can be expected that high levels of photochemical smog are being reached today in the Greater Cairo area and even higher levels in the near future. This is a report of the results of ozone measurements performed in Greater Cairo in the years 1990 and 1991.

Experimental

In 1990 a measurement campaign of three weeks duration, from March 1 to 21, was conducted. Three sites at slightly elevated altitudes in different parts of Greater Cairo had been selected. Since the prevailing wind direction in Cairo is north-east, one station was set up in the industrial area of Shoubra El-Kheima in the north of Cairo at 80 m height on the roof of a large building. The second station was erected at the steep edge of Mokattam Hill, 205 m above sea level, on the roof of a private house. This station is 9 km at distance south of Shoubra. The third measuring site was again 18 km south of Mokattam Hill at 114 m above sea level at the meteorological observatory in Helwan. The three sites are indicated on the map of Cairo in Figure 1.Thus, the three stations cover a north-south distance of 27 km over Greater Cairo.

Ozone was continuously monitored at the three stations using commercially available ozone monitors (Dasibi, Type 1008 AH and 1008 RS). Before and after the measurement campaign, the ozone analysers were calibrated against the 1008 PC ozone generator (Dasibi) used as a transfer standard which was calibrated in Germany, using the neutral potassium iodide method [4]. The ozone analysers together with data loggers (Campbell Scientific, model 21 X) were placed in white painted wooden weather huts. The teflon inlet tube was attached to a pole about one metre away from the nearest surface. All data were collected as five minutes averages in the data loggers and transferred once every week by a buffer module to a personal computer for further processing. Unfortunately, the last transfer of ozone data measured over six days from Mokattam Hill failed. Meteorological data of wind velocity and wind direction, temperature and solar irradiation were measured at the Meteorological Observatory in Cairo at El Kobba as well as at the Helwan meteorological station (see Fig. 1).

In 1991 ozone was measured at one site, on the roof of the Meteorological Observatory in El-Kobba, from the beginning of April until the end of October. A new ozone analyser (Environnement SA, model O_3 41M) was used in combination with a data logger. This half-year period of continuous ozone monitoring in 1991 was divided into three terms:

Term I: April 7 - May 31,
Term II: June 17 - July 25,
Term III: September 9 - October 30.

After each measuring term the ozone analyser was recalibrated.

Results and discussion

The geographical location of the City of Cairo, about 120 km south of the Mediterranean coast, is at 30° N. Greater Cairo is located between two hills of about 200 m height

forming a valley through which the Nile River flows (Fig. 1). The valley may affect the prevailing northerly wind by channelling it along the north-south axis of the valley (s. Fig. 1). The total area of the City of Cairo is about 250 km^2. Since Cairo is surrounded by the Sahara desert in the west and the Eastern desert, the meteorological situation is largely determined by the vast deserts. During the measurement campaign in 1991, from April until the end of October, the atmospheric pressure was remarkably constant. The mean value was 1012 mbar, the minimum was 998 and the maximum value only 1022 mbar. The relative humidity during that period varied steadily between 15 and 85 % during the days and the nights with a mean value of 55 %. This was accompanied by temperature fluctuations between 13 and 42° C, with a mean value of 24° C. A 10 years average indicates that the average total annual precipitation in Greater Cairo is only 29 mm. The prevailing wind direction was northeast, with 63 % during the measuring period in 1991. Spring in Greater Cairo is the season which is characterised by occasional passages of strong hot Khamasin southerly winds loaded with dust and desert sand [5].

Ozone concentration in Greater Cairo during March 1990

The hourly average volume fractions of ozone measured at the three sites (Shoubra El-Kheima, Mokattam Hill and Helwan) in Greater Cairo during March 1990 are shown in Figure 2. The daily formation of ozone in the early morning hours and the fairly rapid decrease in the later afternoon at about 1800 LST result in the typical sinusoidal curves of the diurnal ozone formation, as depicted in Figure 2, due to the photochemical smog cycle [6, 7]. Since according to Singh et al. [8] typical ozone concentrations in clean remote atmospheres range from 20-40 ppb, concentrations above 40 ppb are undoubtedly anthropogenic or "man-made" ozone levels. Ozone production results from the photochemical reaction of the primary pollutants NO_X (NO and NO_2) and unburned hydrocarbons from industry, traffic and thermal power plants. In the evening and at night, ozone is destroyed by NO generated locally by these sources. In Figure 3 the distribution of ozone concentrations measured at the three sites in Greater Cairo is given in the form of histogrammes on the left side and on the right side the average diurnal behaviour of the ozone concentrations over the three weeks of the measurement campaign is indicated. Since normal Gaussian distribution does not apply to the diurnal behaviour of atmospheric ozone concentrations in an urban environment, the data obtained in Cairo were analysed using robust statistical methods [9, 10]. In Table 1 the maximum and minimum values of the ozone concentrations at the three sites are given for the day-time hours from 800 until 1800 LST hours - the time span of photochemical ozone production - and from 1800 LST through the night until 800 LST for the time span of ozone destruction.

Table 1

Maximum, minimum, mean and standard deviation of the ozone volume fractions in Greater Cairo during March 1990

Location /Time	N	O_3max [ppb]	O_3min [ppb]	O_3mean [ppb]	σ [ppb]
Shoubra	428	69	8	34	14
8-18 LST	194	69	8	41	13
18-8 LST	234	55	8	28	11
Mokattam	313	71	3	35	13
8-18 LST	139	71	8	43	12
18-8 LST	174	47	3	28	10
Helwan	422	90	12	45	11
8-18 LST	181	90	16	50	11
18-8 LST	234	70	12	41	10

N = number of data (hourly averages)

High ozone concentrations were monitored at all three sites (s. Fig. 2) reaching 90 ppb in Helwan. The average ozone concentrations take comparable values in Shoubra and Mokattam Hill, as depicted in Figure 3 and shown in Table 1. But at Helwan, approximately 20 km south of Central Cairo, the mean ozone concentrations are higher both at day-time and in the night (see Fig. 3 and Table 1). The average night-time concentration of ozone is significantly higher at Helwan. The reason is that there are no fast-acting sinks, destroying ozone so that the average night-time concentration of ozone is maintained at 40 ppb at that site. The prevailing wind directions in March 1990 were north-northeast during 87 % of the time. Thus, photochemically produced ozone generated in the industrial zone north of and in Central Cairo is transported southward. Generally, the ozone maximum at Helwan occurs with a delay of 1 to 2 hours compared to the City of Cairo. On March 13 and 14, the ozone maximum concentrations at Shoubra and Mokattam were 70 ppb at 1400 LST in the afternoon; at Helwan they were 85 and 90 ppb, respectively, at 1600 LST. On both days strictly northerly winds with wind velocities of 9 and 8.5 km/h, respectively, were blowing so that the transport times for the distance from the City of Cairo to the measuring site in Helwan were 2 hours.

Since ozone in urban air is formed as a result of fast photochemical reactions which, however, need some time, its concentration in ambient air is often correlated with solar irradiance [6, 7, 11]. The ozone volume fraction data were correlated with the intensity of solar irradiance and by introducing a time shift of one to four hours. In Table 2 the data of such a correlation are given as squared correlation coefficients.

Table 2

Squared corrrelation coefficients (r^2) of ozone volume fractions with the solar irradiance during March 1990

Station	Time shift [h]				
	0	1	2	3	4
Shoubra	0.180	0.372	0.456	0.357	0.165
Mokattam	0.246	0.481	0.581	0.347	0.145
Helwan	0.103	0.201	0.261	0.284	0.233

In Figure 4 the correlation is shown of the hourly average ozone volume fractions, measured at Shoubra, with the solar irradiance. It is interesting to note that the optimum time shift for the correlation at Shoubra and Mokattam is two hours indicating that the primary photochemical process takes place two hours before ozone reaches the monitoring site. Since the values of the squared correlation coefficients at Helwan are much lower and the maximum is reached after three hours, it can be concluded that the generally higher ozone concentrations at Helwan are due mainly to the transport of ozone from regions further to the north in Greater Cairo and are to a lesser extent due to ozone locally generated by the photochemical smog process. This indicates that the northern parts of Greater Cairo, where the main industrial areas are concentrated, are the source of ozone and its precursors.

Ozone concentrations in Cairo during 1991

In order to gain more insight into the seasonal behaviour of the photochemical activity in the air of Greater Cairo, a long-term measurement of ozone together with meteorological variables was started on the roof of the Meteorological Observatory in El-Kobba in early April and terminated end of October 1991 (s. Fig. 1). Figure 5 shows a compilation of the probability distribution of the ozone concentrations measured, represented as histogrammes, and of the average diurnal variations of the ozone volume fractions during the three measuring periods. The diurnal behaviour of the ozone volume fractions in Fig. 5 are shown in a "box and whiskers" presentation [10]. The black squares indicate the medians, the box edges the 25th and 75th percentiles, the bars the 10th and 90th percentiles and the dots the minima and maxima values of the ozone volume fractions. The variation of the ozone concentration is largest in the first term when the wind direction varied more than during the other measurement terms. During the summer term the ozone concentration was higher than during the spring and autumn term. During the summer between 11 and 18 hours the WHO air quality standard was exceeded 90 % of the time despite the fact that no extremely high ozone concentrations above 120 ppb were measured. In Table 3 the maximum, minimum, mean and standard deviations of the ozone volume fractions in Cairo, at El-Kobba, during 1991 have been entered.

Table 3

Maximum, minimum, mean and standard deviation of the ozone volume fractions in Greater Cairo in 1991

Term	N	O3max [ppb]	O3min [ppb]	O3mean [ppb]	σ [ppb]
I (Apr. 7 - May 31)	1234	121	12	50	16
8-18 LST	576	121	16	60	14
18-8 LST	658	76	12	41	12
II (June 17 - July 25)	812	105	11	52	20
8-18 LST	365	105	16	67	16
18-8 LST	447	95	11	41	14
III (Sept. 9 - Oct. 31)	1098	96	14	50	16
8-18 LST	488	96	14	62	13
18-8 LST	610	74	25	41	10

N = number of data (hourly averaged)

In Table 3 again the day-time and night-time values of the ozone concentrations are separately indicated. As shown in Figure 5 and in Table 3, the mean ozone concentration over six months, from April until the end of October, was constant, with values of about 50 ppb. Also the day-time and night-time concentrations of ozone are fairly constant throughout the year. These constant average ozone concentrations throughout spring and summer are associated with very uniform meteorological conditions such as high solar insolation and prevailing northerly winds. From April until October, the maximum of the average diurnal ozone concentrations increases from term I, 67 ppb, to only 78 ppb in term II (June-July). Term II is the time when the longest days occur with most intense sunlight for photochemical smog production. From June/July until the end of October, the maximum of average diurnal variations in the early afternoon decreases only slightly to 72 ppb of ozone. The highest ozone concentration of 121 ppb in 1991 was measured on April 23. The constant mean ozone concentrations in Greater Cairo from the beginning of April until the end of September indicate that unlike to the photochemical smog potential in Central Europe the spring and summer ozone dosages in Cairo are surprisingly high and constant. This may mean that the health hazard and crop damage are higher in and around Greater Cairo than in Central Europe during the fairly short period of intense photochemical smog formation from June until the end of August; in other words, the annual integrated ozone exposure is higher in Greater Cairo than in Central Europe.

In spite of the evidently high emission rates of primary pollutants in Greater Cairo and the strong solar irradiance throughout spring and summer, ozone does not reach extremely high concentrations in ambient urban air of Cairo as might be anticipated. Higher ozone concentrations in the eastern Mediterranean were measured at Athens, Tel-Aviv and Jerusalem [2, 12, 13]. One explanation for the lower maximum ozone concentration in Greater Cairo might be the steady wind blowing almost exclusively from the north to northeast throughout the year (see Fig. 6). When we examine more closely the wind on the day 22 April when the ozone volume fraction exceeded 120 ppb (see Fig. 7), we see that on that day the wind speed was unusely low and in addition that the prevailing wind direction was from the west and northwest. Assuming that the wind monitored at the Meteorological Observatory at El-Kobba is representative for the neighbouring region of about 20 to 30 km in radius, we can calculate the back-trajectories for the time preceding the daily peak ozone concentration. They show the probable routes the air travelled before reaching the monitoring site at El-Kobba. These trajectories are shown in Figure 8 for the three days of Figure 7. While the trajectories for the 21st and 23th April represent the typical situation in Cairo, the one for the 22nd April is markedly different and showing that the air reaching the monitoring site spent about 7 hours within a radius of 20 km, while typically spends significantly less than 2 hours within that distance. This steady flow of air in one direction might also explain the relatively high nocturnal ozone concentrations observed in Cairo. They might rather be representative of the background air to the northeast of the city. On the other hand this also means that the urban plume of Cairo will have the largest effect in the area to the southwest in the agricultural region of El Faiyoum.

Egypt has fixed ambient air quality standards for many gaseous and particulate components. They have been laid down as 24-hour mean values with a maximum permissible level which shall not be exceeded. Surprisingly, the ambient air quality standard for ozone of 30 ppb is much lower than usual international air-quality standards, like the value of 30 ppb for an eight hour period or 60 ppb for a one-hour period of the WHO or the German recommendation of 90 ppb for one hour. If we accept the stringent

WHO long-term target value of 60 ppb of ozone not to be exceeded for one hour, this ozone level had been exceeded in measuring term I for 6 hours per day, in term II for 9 hours per day, and in term III for 7 hours per day (see Fig. 5). For the Greater Cairo area we have to conclude that the air-quality standard for ozone is too low and should be reviewed and reformulated taking into account international standards.

Contrary to many urban areas in Europe and the USA, the average night-time concentrations of ozone are above 30 ppb (s. Figs. 3 and 5) in Greater Cairo. In general, in urban areas high NO concentrations caused by traffic destroy the high ozone levels of the afternoon [6]. In Greater Cairo wind speeds during the night throughout 1991 were high, generally betwen 4 and 7 ms^{-1}, blowing predominantly from the north. Thus at night all NO from the evening rush hour could be swept away from the urban centre and ozone from the desert with average concentrations of 30 ppb were monitored at night at the El-Kobba site. The fairly high night-time ozone concentrations could also be explained by the particular location of Greater Cairo. Cairo is surrounded by deserts. Very stable atmospheric conditions with the formation of a shallow nocturnal inversion level occur regularly every day, causing a strong increase in the relative humidity from about 30 % to about 80 % in the night. Thus, it is likely that our measuring sites in Greater Cairo were located above the nocturnal inversion layer. Above the nocturnal inversion layer, the ozone formed during the day is effectively cut off at night from all sinks below the inversion which gives rise to generally higher average night-time concentrations of ozone. The measurement of vertical profiles of ozone, temperature and humidity in Cairo at night using a captive tethered balloon will clarify this assumption.

Conclusions

From the analysis of the ozone concentrations measured in the Greater Cairo area in 1990 and 1991 the following conclusions are drawn:

- The regular diurnal variations of the ozone concentration with peak values of up to 120 ppb in the afternoon indicate a strong contribution of photochemical smog and are similar to those reported from other urban centres in Europe and North America.

- Ozone is formed predominantly over the industrial area and in the centre of Cairo and transported southward by the prevailing northerly winds.

- The daily maximum values of the ozone concentration in the Greater Cairo area have approached, but not yet exceeded, critical levels. However, unlike in many urban centres in Europe, the daily mean ozone concentration of 50 ppb throughout the year is higher in Greater Cairo.

- Different from many urban centres in Europe and North America, fairly high average ozone concentrations of 40 ppb are observed during the night throughout the year.

- The very low Egyptian air quality standard for ozone should be reconsidered.

Acknowledgement

This work was performed within the framework of a German-Egyptian agreement on scientific co-operation. The authors wish to thank for the funds granted by the German Federal Ministry for Research and Technology, represented by the International Bureau of the Forschungszentrum Jülich (KFA), and by the Egyptian Ministry of Research.

We also gratefully acknowledge the untiring support and interest of Prof. F.H. Hammad of the Egyptian Atomic Energy Authority.

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Figure Captions

Fig. 1 Map of Cairo with the monitoring sites and height contour lines
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Fig. 2 Hourly average ozone volume fractions at three measuring sites in Greater Cairo during March 1990.

Fig. 3 Probability distribution of hourly average ozone volume fractions (left) and their average diurnal variations (right) at the three measuring sites during March 1990.

Fig. 4 Correlation of hourly average ozone volume fractions at the Shoubra site with the intensity of solar irradiance without time delay (top) and with a time shift of 2 hours (bottom).

Fig. 5 Probability distribution of hourly averaged ozone volume fractions (left) and their average diurnal variations (right) at El-Kobba during the three measuring periods in 1991. The diurnal behaviour of the ozone volume fractions are given in a "box and whiskers" presentation [10]. For explanation consult the text.

Fig. 6 Wind roses for the three monitoring term in Cairo during 1991 at El-Kobba:
top 7 Apr. - 31 May; centre 17 June - 25 July; bottom 9 Sept. - 30 Oct.

Fig. 7 Diurnal variation of the wind data and ozone volume fractions for 21 - 23 April 1991. In the top diagram the upper curve gives the wind direction as indicated on the right and the lower curve the wind speed on the left scale.

Fig. 8 Air mass trajectories calculated backwards from the peak ozone values of 21, 22 and 23 April 1991 in Greater Cairo at El-Kobba. The distances between adjacent points correspond to one hour intervals.

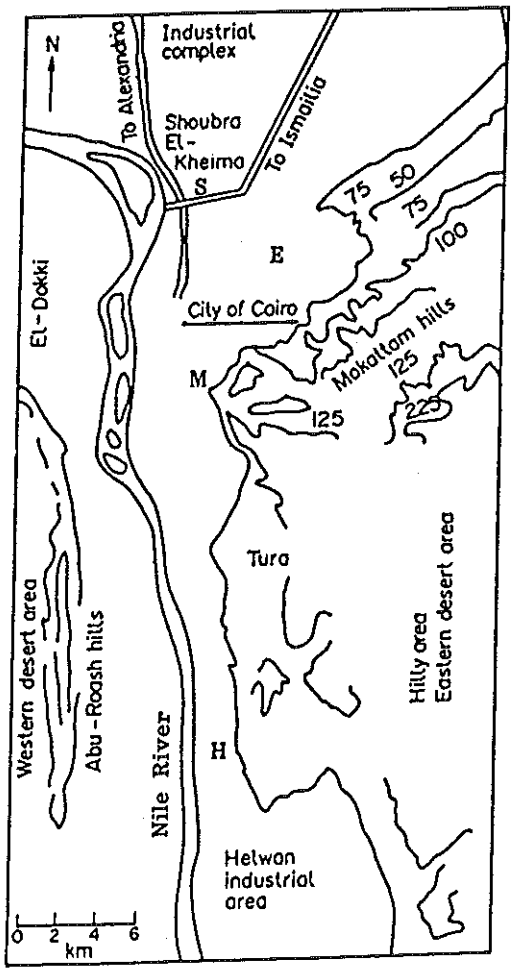
N
Industrial complex
To Alexandria
To Ismailia
Shoubra El-Kheima
S
E
M
H
75
50
75
100
125
125
125
El-Dokki
City of Cairo
Mokattam hills
Tura
Western desert area
Abu-Roash hills
Nile River
Hilly area
Eastern desert area
Helwan industrial area
0 2 4 6
km

Figure 1

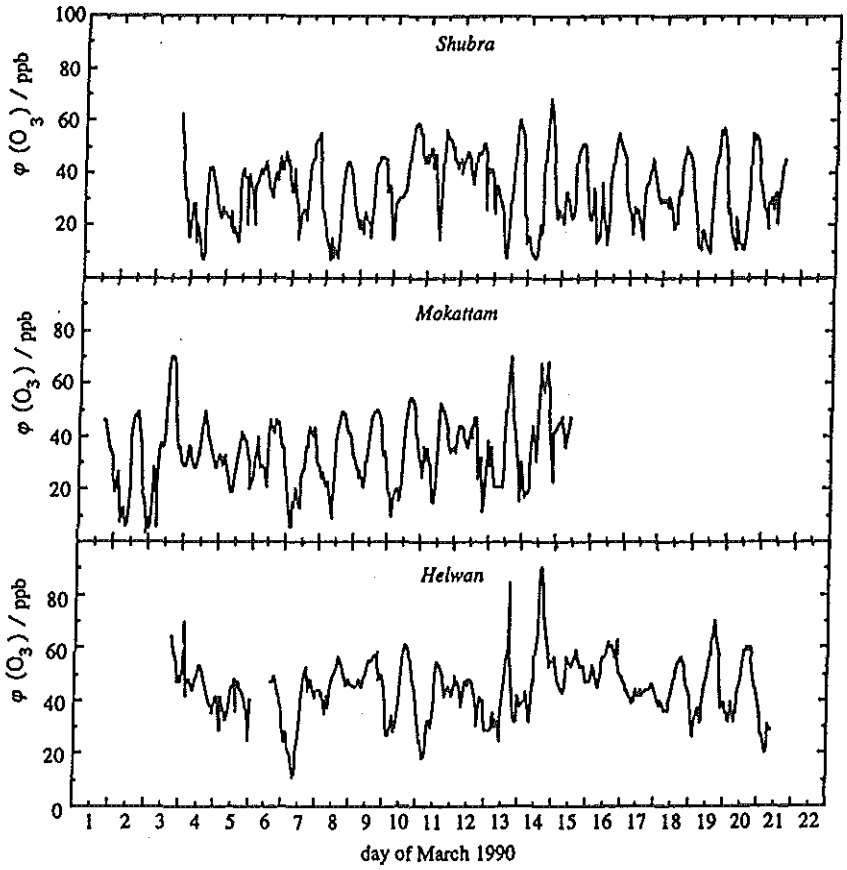

Figure 2

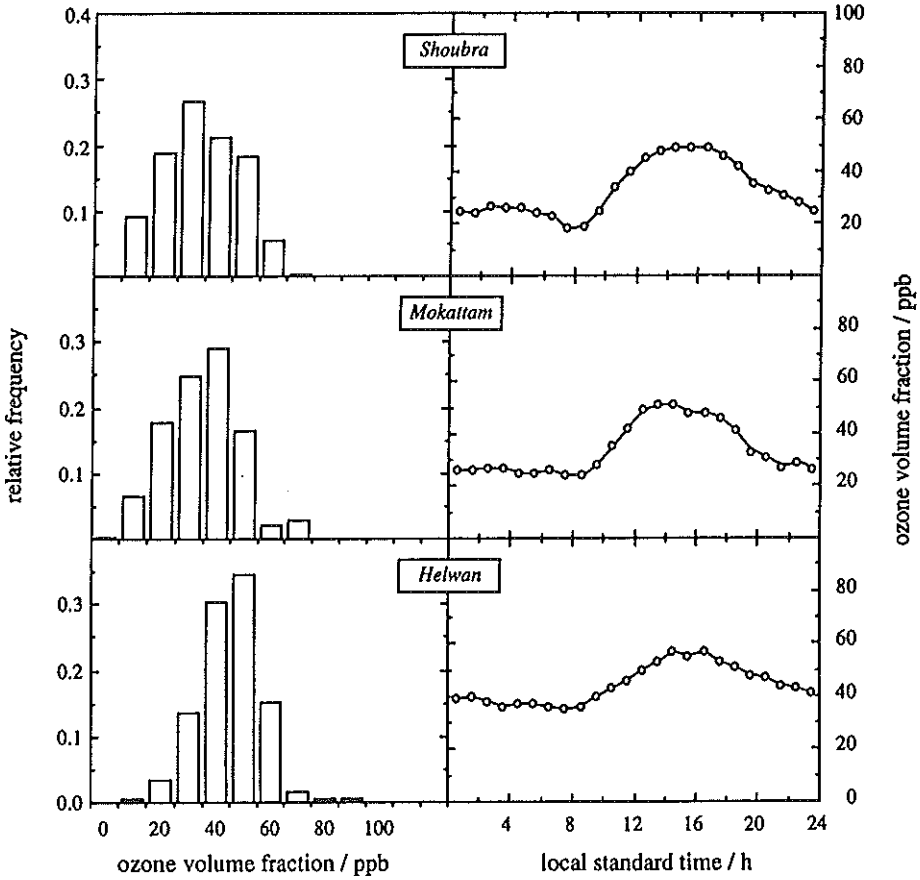
Shoubra
Mokattam
Helwan
relative frequency
ozone volume fraction / ppb
ozone volume fraction / ppb
local standard time / h

Figure 3

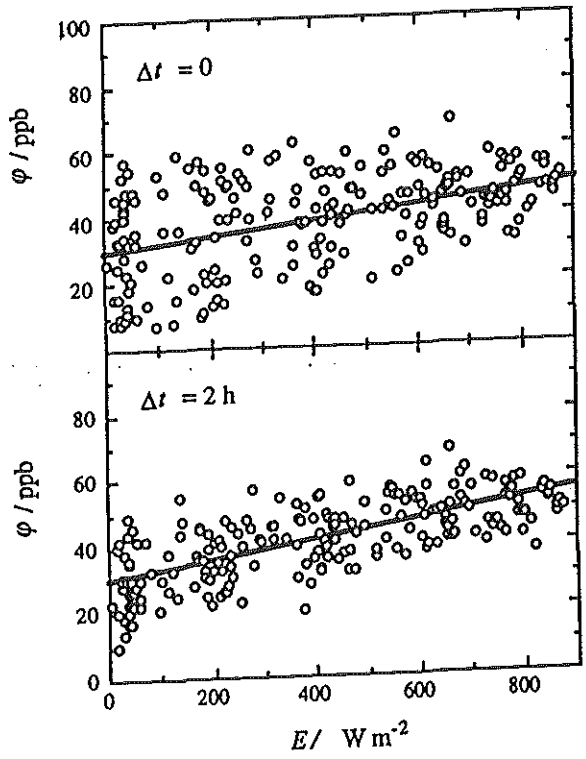
Δt = 0
Δt = 2 h
φ / ppb
φ / ppb
100
80
60
40
20
80
60
40
20
0
0
200
400
600
800
E / W m-2

Figure 4

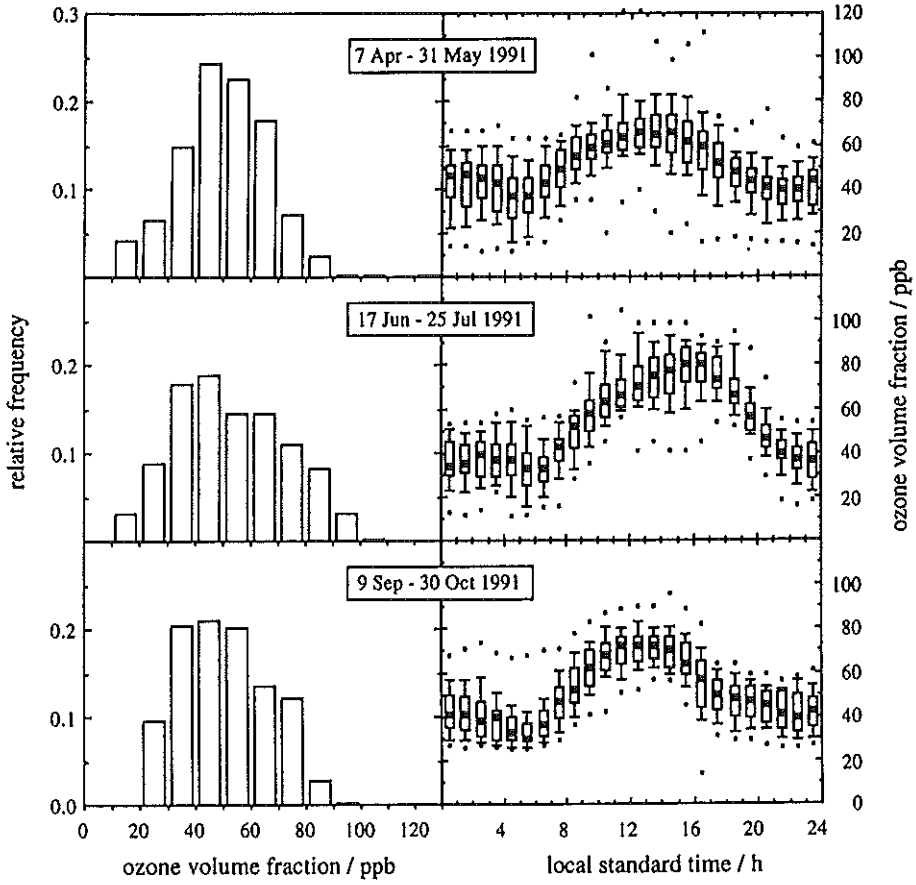
7 Apr - 31 May 1991
17 Jun - 25 Jul 1991
9 Sep - 30 Oct 1991
relative frequency
ozone volume fraction / ppb
ozone volume fraction / ppb
local standard time / h

Figure 5

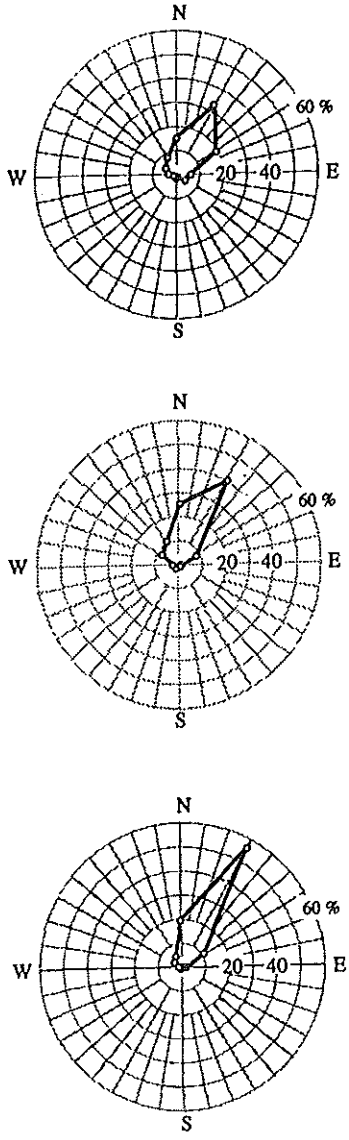

Figure 6

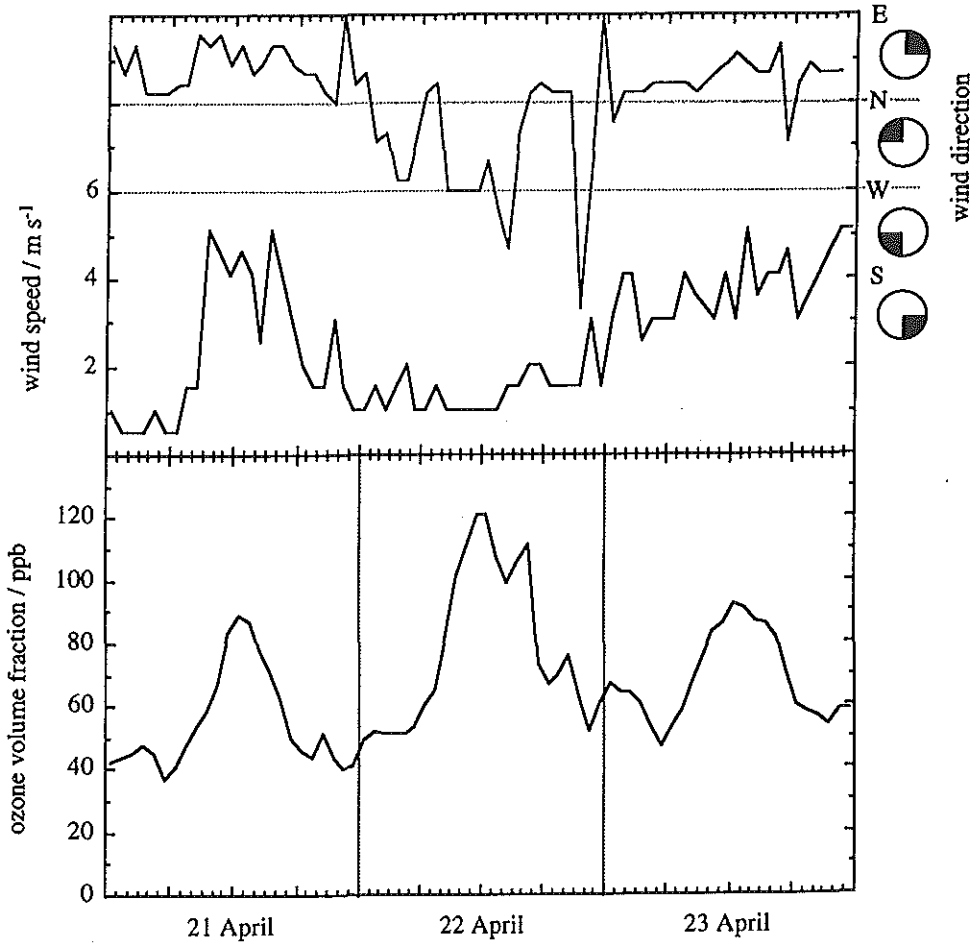
E
N
W
S
wind direction
wind speed / m s-1
6
4
2
ozone volume fraction / ppb
120
100
80
60
40
20
0
21 April
22 April
23 April

Figure 7

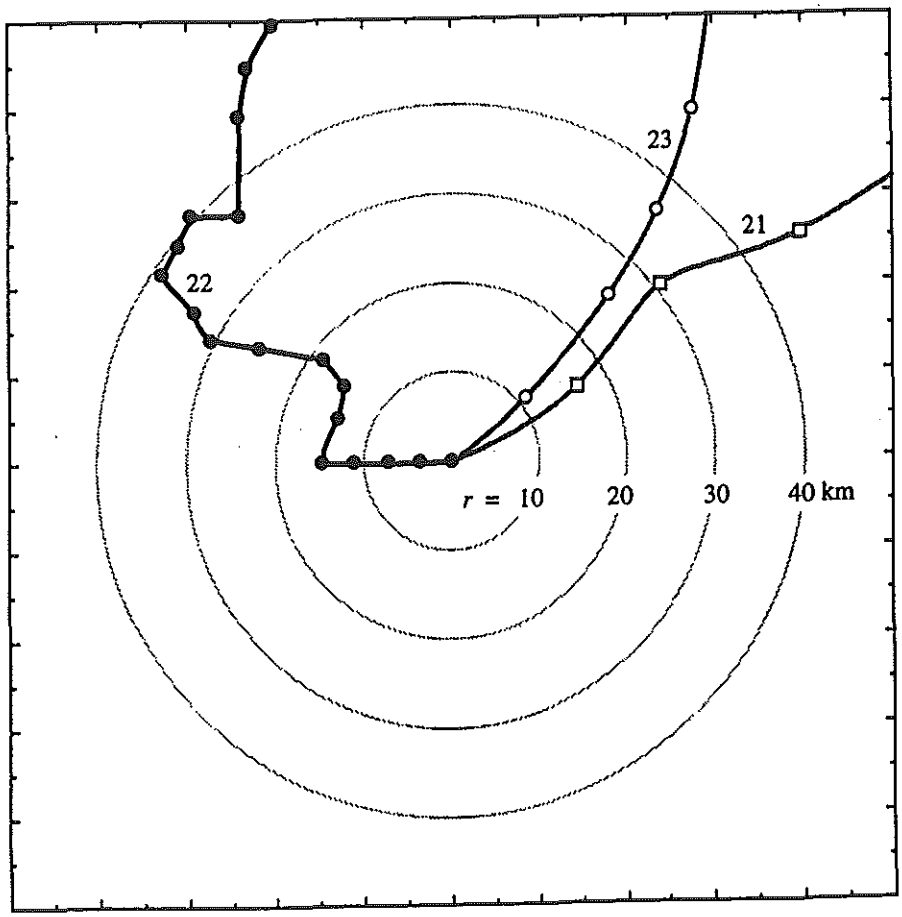

Figure 8

Ozone in the Western Desert of Egypt

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Abstract

Ozone was continuously monitored in the Western Desert of Egypt 30 km south of the Oasis Dahla from March 24 until April 9, 1993. Surprisingly high ozone concentrations up to 60 ppb were monitored when northerly winds prevailed. On March 27 and 28, when southwesterly winds were blowing, the ozone concentration was lower with a daily maximum of 40 ppb only indicating that today even the remote desert does not represent an area for clean background air.

The vertical turbulent ozone flux as well as the sensible and latent heat fluxes were measured continuously throughout the measurement campaign. While the ozone flux in the night is essentially zero, maximum day-time ozone fluxes of 20 ppb cm s^{-1} were measured yielding a maximum daily dry deposition velocity of 0.30 cm s^{-1}. This indicates that the ecosystem desert represents a larger sink for tropospheric ozone than previously assumed.

Introduction

Ozone is produced photochemically in the stratosphere from where it is mixed down into the troposphere. Finally, ozone is destroyed at the earth's surface which is the most important sink for this natural trace gas. The rate of ozone destruction differs with the type of surface. Since 18% of all land surfaces on earth are deserts, there is interest to quantify the amount of ozone deposited to the ecosystem desert. Furthermore, attempts are often made to distinguish between ozone concentrations in anthropogenically polluted areas and so-called natural background concentrations of ozone which should exist in clean remote areas. The assignment of a hypothetical natural background concentration of ozone is rather ambiguous because through long-range transport of polluted air masses ozone and its precursors (NO_x and hydrocarbons) can be advected over hundreds of kilometers. Nevertheless, the western part of the Egyptian desert is likely an

area where the natural background concentration could be measured. Within a German-Egyptian Research Project a remote area approximately 30 km south of the Oasis Dahla (29°04' N, 25°13' E), some 650 km south of the Mediterranean coast was selected as measuring site.

Site description and instrumentation

The selected desert site was a flat sandy area with a favourable upwind fetch of about 30 km to develop a constant flux layer of air in the surface layer. This is necessary to access the rate of direct ozone deposition to desert sand utilising the so-called eddy correlation technique (Hicks and Wesely, 1978; Fowler and Duyzer, 1989). The successful application of the eddy correlation or covariance technique requires the simultaneous measurement of the ozone concentration and of the vertical wind velocity by fast-response sensors. The instruments consist of a three-component sonic anemometer (Kaijo Denki DAT 310,) for wind and temperature and a novel fast-response ozone sensor (Güsten et al., 1992a). Both instruments are mounted on the top of a lean tower in 5.5 m height. The ozone flux is computed on-line in the desert as the covariance of the fluctuations of the ozone concentration with the fluctuations of the vertical wind velocity. For details on the instrumentation and methodology of the eddy correlation technique the reader is referred to the literature (Haugen, 1973; Stull, 1988; Güsten, 1992b).

The rapid measurement of the humidity is based on the UV-light absorption of the krypton ultraviolet emission by water vapour at 123.58 mm. A commercially available krypton lamp (KH20, Campbell Scientific Ltd.) was used in combination with a datalogger (21X Micrologger, Campbell Scientific Ltd.). All data of the fast-response sensors were measured with 10 Hz time resolution and the flux calculations were processed on-line. All data are finally stored in a laptop computer.

The whole system for eddy flux measurement (fast-response-Kr-lamp and ozone sensor, ultrasonic anemometer and conventional ozone analyser) was powered with a photovoltaic generator system of 6 m^2 total area of photovoltaic cells providing 1100 W.

Results and discussion

Ozone concentrations in the desert

Ozone was continuously measured in the desert from March 24 until April 9, 1993. In Figure 1 the diurnal behaviour of the ozone concentration is shown for the whole measuring period. With the exception of two days on March 26 and 27,

surprisingly high ozone concentrations up to 60 ppb were recorded as daily maximum values. Contrary to many urban areas in Europe and the USA, the average night-time concentration is very high and minimum values in the night are rarely below 35 ppb.

In urban areas high NO concentrations caused by traffic, destroy the ozone levels of the afternoon. Thus, in these areas often night-time concentrations near zero are measured. Since there is no photochemical activity in the night that could produce ozone locally, it can be argued that night-time concentrations of 35-40 ppb could be regarded as natural background concentrations. However, as can be seen in Figure 1 on March 26 and 27, night-time ozone concentrations dropped to 20-24 ppb. Nearly on all days of the measurement campaign prevailing northerly winds were registered with the exception of the two days, March 26 and 27, when the wind was strictly southwest coming from Sahara Desert. The hot wind from the Sahara transports markedly drier air to the measuring site as is depicted in Figure 2. On March 26 and 27 as well as for half a day on April 1 the humidity dropped to values below 2 g m^{-3}.

Thus, it is conceivable that the northerly winds still transport some polluted air masses. Only when the wind is coming from southwest out of the Sahara unpolluted air masses are transported to the measuring site and the natural background concentration can be measured. According to Singh et al. (1978) typical ozone concentrations in clean remote atmospheres range from 20-40 ppb. The polluted air masses coming from NW where Lybian and Egyptian oil fields are located, may transport air pollutants such as NO_x and hydrocarbons which form ozone during their long-range transport with the prevailing northwesterly winds. Contrary to this, the southwesterly winds from the Lybian and Chad desert should be not contaminated with the precursors for ozone formation. Thus, from this major wind direction only air masses with the natural background concentration of ozone reach the measuring site south of the Oasis Dahla.

Eddy fluxes of ozone to the desert

As early as 1874 (Zittel, 1874) ozone was first measured in Egypt using the qualitative method of Schönbein. Zittel observed that the ozone concentration was usually higher in the desert than in the Nile Valley, which he attributed to the different surface properties. In Figure 3 the diurnal behaviour of the vertical turbulent ozone flux to the ecosystem desert is shown for the time of the measurement campaign. While during the night the ozone flux is essentially zero, daily maximum values of 20 ppb cm s^{-1} were measured. Common custom is to express the

rate of the dry deposition of a trace gas as a deposition velocity (Stull, 1988). The dry deposition velocity V_d is defined as the vertical flux F_c of a pollutant devided by the atmospheric concentration c at a specific height above the receiving surface, normally in one meter height:

$$V_d = - \frac{F_c}{c} \; [cm\, s^{-1}].$$

In Figure 4 the deposition velocities of ozone to the desert are summarized for the whole measuring period. Daily maximum values of 0.30 cm s^{-1} are surprisingly high for the dry deposition velocity of ozone to sand. Since there are no data in the literature for sand, the deposition velocities can only compared with dry deposition velocities of ozone to bare soil. Wesely et al. (1981) reported a maximum deposition velocity of 0.1 cm s^{-1} for bare soil well saturated with water, while Turner et al. (1973) give higher values of slightly less than one cm s^{-1}. Since it appears that the dry deposition velocity of ozone is a function of soil moisture content, our maximum value of 0.30 cm s^{-1} seems appropriate for dry desert sand. Over the whole measuring period of 16 days from March 24 to April 9 a mean deposition velocity of V_d = 0.07 cm s^{-1} is calculated and recommended for global models considering the sources and sinks of ozone in the troposphere.

Acknowledgement

This work was performed within the frame work of a German-Egyptian agreement on scientific co-operation. The authors wish to thank the International Bureau of the Forschungszentrum Jülich (KFA) and the Egyptian Ministry of Research for funding the project.

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Figure Captions.

Fig. 1 Half-hourly average volume fractions of ozone in the Western Desert of Egypt, meaured 30 km south of the oasis Dahla in 1993.
82 Julian day = March 23
99 Julian day = April 9

Fig. 2 Diurnal variation of the humidity in the Western Egyptian Desert from March 24 to April 9, 1993.

Fig. 3 Diurnal variation of the vertical turbulent ozone flux in the Western Egyptian Desert from March 24 to April 9, 1993.

Fig. 4 Diurnal variation of the dry deposition velocity of ozone to the Western Egyptian Desert from March 24 to April 9, 1993.

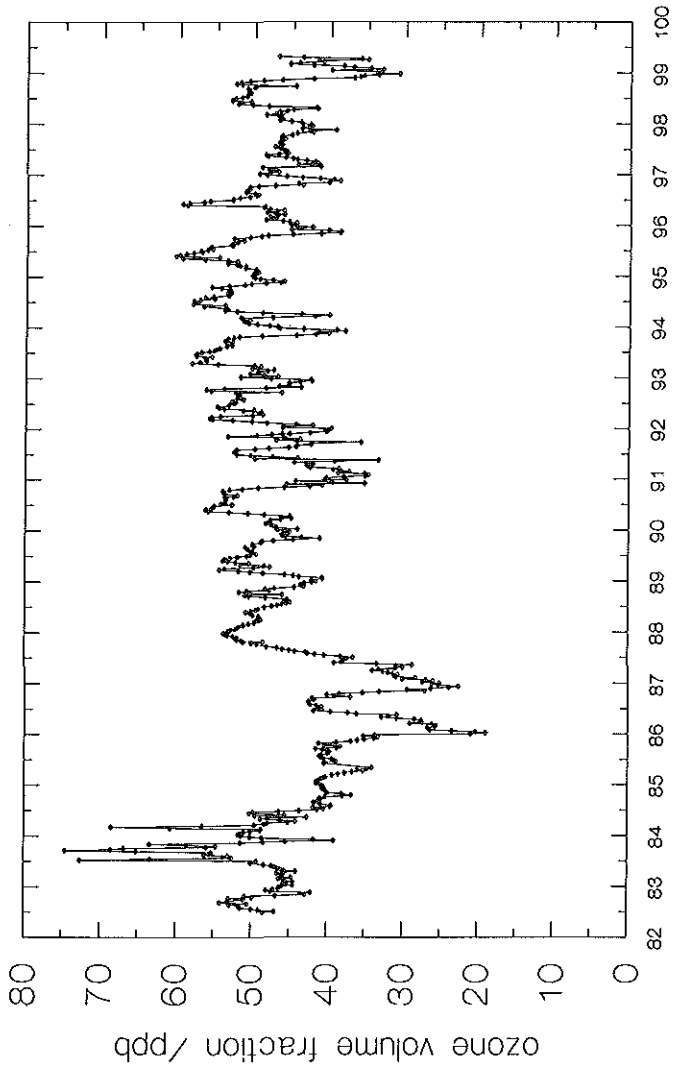
ozone volume fraction /ppb
0
10
20
30
40
50
60
70
80
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
julian day 1993

Figure 1

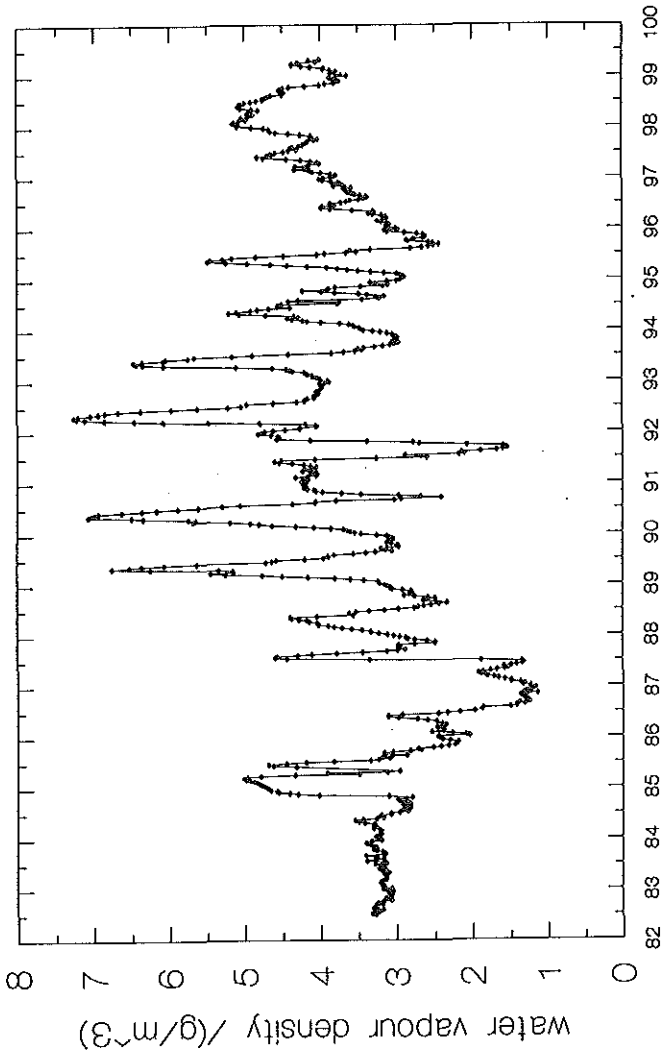
water vapour density /(g/m^3)
0
1
2
3
4
5
6
7
8
julian day 1993
82
83
84
85
86
87
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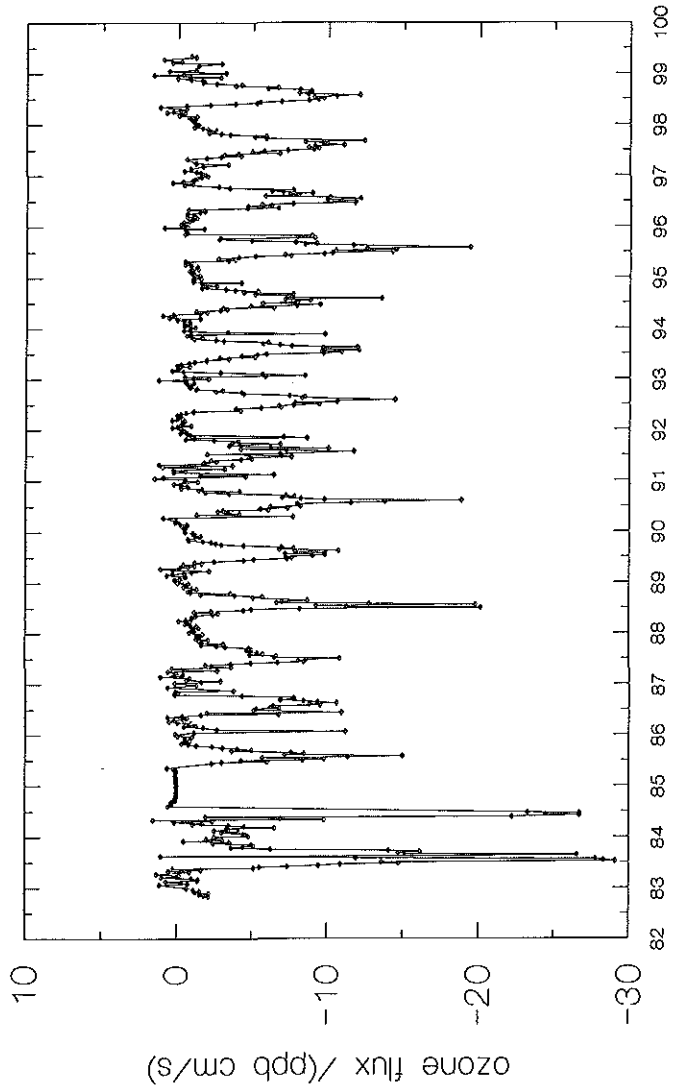
Figure 2


ozone flux /(ppb cm/s)
10
0
-10
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-30
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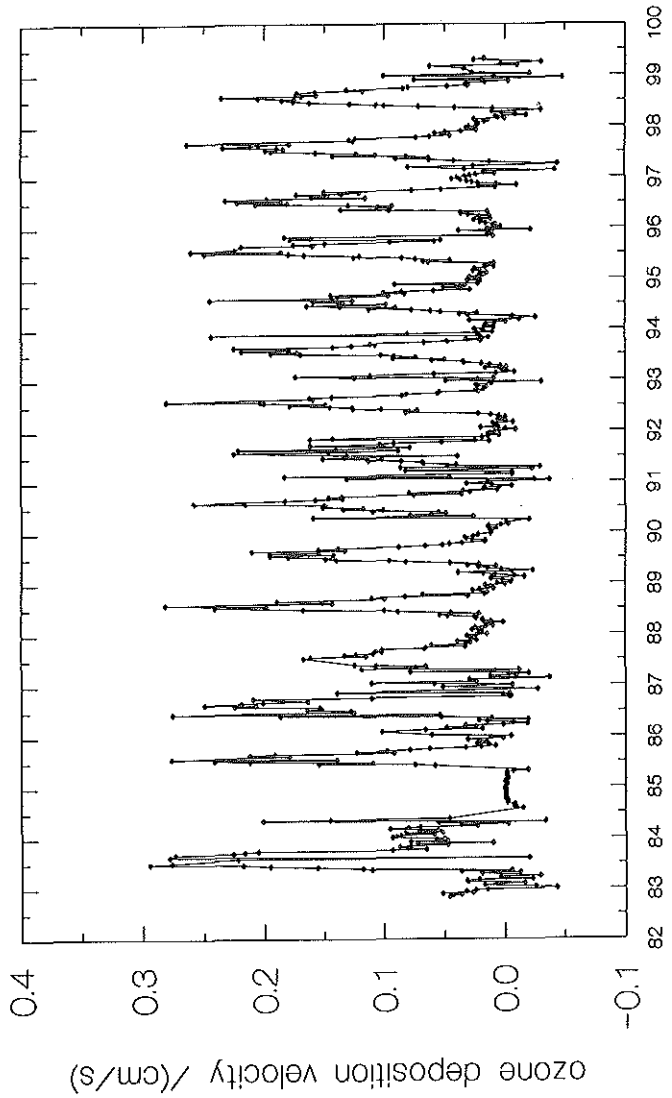
julian day 1993

Figure 3


ozone deposition velocity /(cm/s)
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0.3
0.2
0.1
0.0
-0.1
julian day 1993
82
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84
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Figure 4

KFA - Jülich
ZFK-DE

The LAWI Plant: An Instrument for Waste Reduction with Minimized Environmental Impact

Stephan Halaszovich

German-Egyptian Seminar on Environmental Research

Cairo, March 21 to 23, 1994

In the years after 1965 it became more and more evident that there was a demand for a effective system to treat the combustible solid radioactive waste that was generated in the laboratories and the research reactors at the Juelich Research Centre KFA. Different incinerator systems were already known, but none of them was considered optimal for this kind of waste. Although it has to be preselected to sort out non burnable materials by collecting it in separate bins it has the most varied properties still containing different kinds of materials such as glass and metals.

In order to find a better solution for the incineration of this kind of waste the development of a new incineration process, which became the Juelich Incineration Process, was started in 1969. The result was a multi step process with the following basic design characteristics:

- direct feed of the waste as being collected in the laboratories without further pretreatment,
- separation of the different stages the materials generally undergo during combustion for better process control,
- minimisation of aerosol discharge into the off-gas system, best possible burnout of the ash,
- keep the radioactivity of the scrub solution below exemption limit.

The first Juelich Incinerator was assembled in 1972 and commissioned with nonradioactive waste. After extensive testing and trial runs it was licensed for the treatment of radioactive waste in 1976.

After ten years of successful operation it has been replaced by a new incinerator JUEV 50 which has been commissioned by the company Kraftanlagen AG Heidelberg. First radioactive waste was treated in the new plant in November 1988.

The experience with successful operation has been presented at a seminar in Inshass Research Centre on the occasion of the inauguration of the Low Active Waste Incinerator LAWI in December 1983 by Halaszovich (1).

The LAWI plant has been built and started in a close and very fruitful cooperation between the Inshass Research Centre and KFA Juelich. A detailed description of this plant is given by Krug, Thöne, Schmitz and Abdelrazek (2).

The first results in the incineration of non radioactive simulated waste with LAWI are presented at this seminar by Ahmed and Abdelrazek (3).

CHARACTERISTICS OF THE WASTE

Table 1 shows the mean composition of the waste which has been treated at KFA.

Components	Portions	
	Nominal (Weight %)	Average 88-92 (Weight %)
Woods	10	2
Paper	10	7
Plastics (PVC)	18 (3)	13
Animal carcasses	5	4
Filters	7	14
Sludge	15	14
Dried evaporator concentrate	15	10
Metals	10	36
Mixed materials	10	36

TABLE 1: MEAN COMPOSITION OF THE MISCELLANEOUS WASTE

The discrepancy between the nominal values and those listed by the operator for woods, paper and filters is due to the fact that in practice the total weight of the filters is measured including wooden and paper structures. Concerning mixed materials it is not possible to express in figures the portion of each ingredient exactly. As no further sorting of the material is performed beyond separate collection the figures are only estimated by visual control in the glove box.

Although the design criteria originally did not include the treatment of compacted material, it can be treated as well.

The waste composition as shown in table 1 is expected to be similar to the radioactive waste generated in Inshass Research Centre and it is very similar to municipal solid waste. Obviously it is very heterogeneous, containing materials with high and low calorific value. Thus using an ordinary shaft furnace the temperature would fluctuate to the changing calorific value of the waste components and consequently the off gas composition could not be kept within optimum range. The same effect is observed when the cold feed material directly drops into the fire zone of a shaft furnace.

SPECIAL FEATURE OF LAWI

LAWI is operating on the principle of the Juelich Thermoprocess as shown in figure 1. The essential of this process is that the material is slowly flowing from the cold upper part to the hot lower part of the gasification chamber thus being heated up uniformly. At the grate level it glows and is being gasified at about 800°C. All solids and gases are passing through this zone. The temperature is very stable and consequently the off gas composition also. All organic compounds are destroyed due to the high temperature and the long residence time in the combustion chamber. No smoke or soot comes to the filters. Non combustible particles are retained by the filters. If necessary a scrubber can be added to the off gas purification system to trap chlorine and fluorine.

Dioxines and furans are partly recombined in the heat exchanger. Recombination can be minimized by sudden temperature drop using a quencher instead of air cooled heat exchanger.

According to the German Clean Air Act (17. Bundesimmissionsschutz-Verordnung, 17. BImSchV) the concentration of Dioxines must be less than 0,1 ng/m^3 in the purified off gas latest by the end of November 1997. In order to meet this requirement additional carbon filters have to be added to the off gas system.

PROPOSED EXPERIMENTS WITH LAWI

LAWI is predestinated by its operating principle to be an incinerator with minimized environmental impact. Nevertheless there is an intensive and wide-ranging experimental program needed to scale up the plant and to optimize its functions with regard to different waste compositions and to current regulations.

It must be decided first what kind of waste should be treated in incinerators like LAWI. Taking into account that there are millions of tons of municipal waste generated every year, it is obvious, that very large single units or a large number of smaller units have to be built to provide sufficient incinerator capacity. Therefore scale up is an important question. It is possible to treat several hundred kilograms of material per hour in a unit with LAWI design. But for a throughput of several tons per hour a new design must be created i.e. a technique which allows to transport a big quantity of material through a heat up zone to a uniformly heated glowing bed. The necessary data base like gasification time etc. can be obtained using the LAWI plant.

With regard to smaller plants for the treatment of special waste streams i.e. materials containing hazardous chemicals and radioactive solid waste the data base also has to be generated. The LAWI plant is the ideal tool for the generation of such data. Therefore a

proposal for a LAWI-R & D-Program has been made at the December seminar at Inshass by Krug (4). This proposal has been discussed at a round table and accepted with minor modifications as a working paper.

A detailed program will be worked out by the participants at Inshass Research Centre and KFA Juelich. The four main items of this program are:

1. Dynamic testing of the LAWI plant to study the behaviour at normal conditions and at limiting operating conditions.
2. Investigation of material balance, of energy balance, of thermo dynamics of the plants components and of possible interactions which would lead to the formation of toxic compounds.
3. Optimization of the operating conditions of the plant and preparation of the operating manual, of the maintenance manual and of the final safety analysis report.
4. Verification of theoretical models.

CONCLUSION

In a successful cooperation between Inshass Research Centre and KFA Juelich the prototype incinerator LAWI with a capacity of 15 kg per hour has been installed at Inshass Research Centre.

LAWI is operated on an advanced principle which allows the combustion of hazardous and radioactive waste with minimized environmental impact.

Prior to the incineration of real radioactive waste LAWI will be used for the generation of the data base which is required for scale up as well as for the purpose of optimization and adaption of this technic to the incineration of different kinds of hazardous materials.

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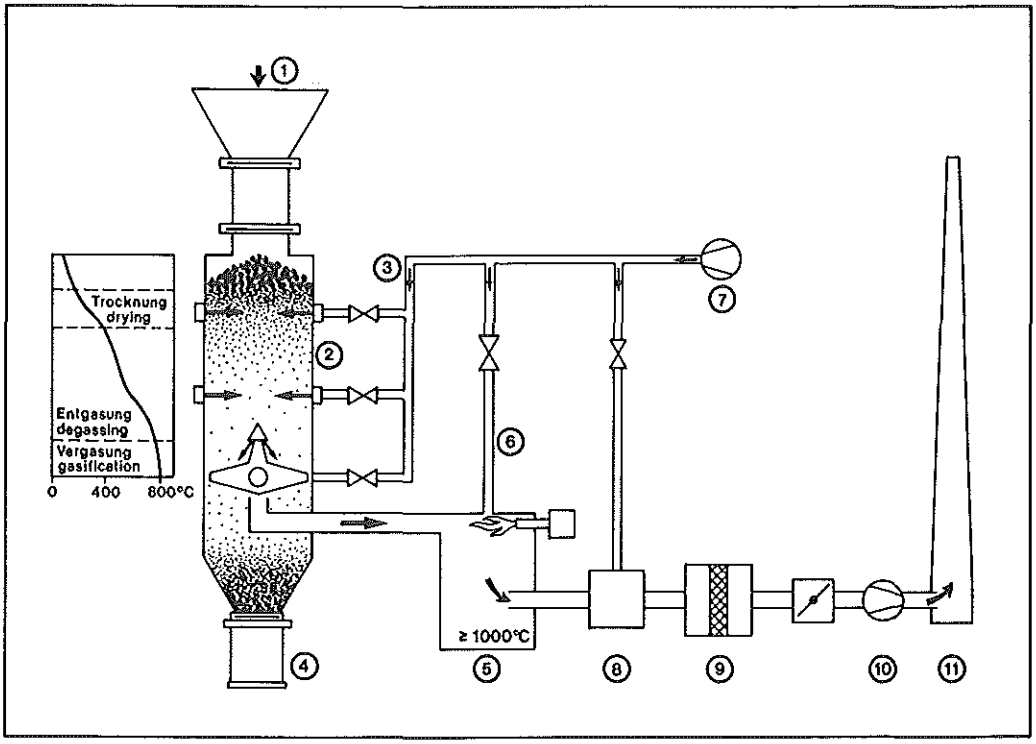
3 Ahmed, A. Z.; Abdelrazek, I. D.: First Results in the Incineration of Burnable Simulated Municipal Solid Waste, German-Egyptian Seminar on Environmental Research, Cairo, March 21 to 23, 1994.

4 Krug, W.: Considerations and Proposals for a LAWI-R & D-Programme, German-Egyptian Workshop on possible R & D Utilization of LAWI for Waste Incineration.



1 Materialzugabe
2 Gasreaktor
3 Vergasungsluft
4 Ascheablaß
5 Brennkammer
6 Verbrennungsluft
7 Frischluftversorgung
8 Abgaskühlung oderWärmenutzung
9 Abgasreinigung
10 Abgasförderung
11 Kamin

Abb. 1 Der Jülicher Thermoprozeß, Funktionsprinzip

1 Material feed
2 Gas Reactor
3 Gasification Air
4 Ash Discharge
5 Combustion Chamber
6 Comcustion Air
7 Air Supply
8 Off-gas Cooling or Heat Utilization
9 Off-gas Cleaning
10 Off-gas Release
11 Stack

Fig. 1 The Jülich Thermoprocess, Operating Principle

FIRST RESULTS IN THE INCINERATION OF BURNABLE SIMULATED MUNICIPAL SOLID WASTE

A.Z. Ahmed , and I.D. Abdelrazek

Nuclear Research Centre ,Atomic Energy Authority,Egypt

Abstract

About 10 million tons of municipal solid waste (MSW) are produced per year in the Arab Republic of Egypt , 98 % of it being landfilled and recycled . The increasing concern over landfills as a waste management option and decreasing availability of sites have focused on incineration process as a powerfull key for the destruction and volume reduction of generated MSW .To protect the environment ,the controlled incineration process must be advanced to such extent that the amount of pollutants released is largely minimized . to achieve this , a comprehensive knowledge is required which has to be provided by scientific search into the fundamental of incineration , flue gas cleaning . The low active waste incinerator (LAWI) facility erected and operated at the Nuclear Research Centre (NRC) ,Cairo , serves to fulfill these research tasks .

1 . Introduction

Municipal solid waste (MSW) is generated in a large quantities in Egypt , particularly in Cairo Greater Area . Methods of disposal currently used cannot ope with the large quantities generated .All of those are becoming more and

more difficult . Due to the undesirable environmental impact of MSW there is a considerable public concern , as long term landfill has inherent liabilities and steadily increasing cost as available sites diminish , and health regulations drive up the operating costs . Except for recycle and reuse opportunities ,the majority of putrecsible and thermallydestructable waste will be composted and incinerated respectively. The use of KFA Juelich incineration process which proved to be successfull in reducing the volumes ofcombustible waste could be a major contribution towards solving this problems .

In the early phase of the proposed study ,the low active waste incinerator (LAWI) , already has been installed and operated at the Nuclear Research Centre (NRC) , Egypt could be utilized for conducting the suggested demonstration trials of a simulated municipal solid waste incineration . The goal pursued being to conduct research work in the field of incineration , flue gas cleaning , and treatment of ash.

2 . LAWI Test Facility

The LAWI semi-industrial test facility is the reseach tool available to the Metallurgy Department where scientific investigations can be conducted into the basic processes of municipal solid waste incineration and treatment of off gas and solid ash residue . The primary goal of these research

activities is aiming at possibility of incineration of MSW especially waste disregarded from composting plants and controlling problems arising from the polluants present in all products streams .

The test facility has been designed for a nominal capacity of 15 kg per hour solid waste . It is fed with a simulated waste of the following composition :

Plastics	50 %
Cellulose	35 %
Rubber	3 %
Humidity	12 %

The LAWI is schematically presented in Fig .1 , as the parts are :

- Glove box and loading station .
- Gas reactor
- Combustion chamber
- Air mixing cooler
- Cyclone separator
- Filter group which includes :
  - Bag filters
  - high efficiency particulate absolute (HEPA) filter
- Exhaust blower (1B1)
- Fresh air blower (2B1)
- Valves and fittings
- Piping and insulation

- Burner and gas feeding system
- Process control instrumentation
- Control panel
- Stack

The gas reactor has to be filled completely with waste via the glove box. During operation , there is a temperature gradient in the waste column as temperature increases from near temperature at the top to 800 C arround the movable grate (see Fig .2) . By addition of under stoichometric amount of air , the waste is dried , decomposed , and then will be gasified . The energy necessary for decomposition and gasification of waste will be obtained from partial oxidation of produced gases . The produced gases from the gas reactor , consisting mainly of carbon mono oxide C O , hydrogen H2 , carbon dioxide C O2 , water vapour H2O , and traces of methane CH4 , as it will be completely oxidized by addition of secondary air to combustion chamber . Ashes and coke are falling through the grate to the bottom of gas reactor where it may be burned out by addition of air. Also gasification of coke as well as tar may be conducted in the combustion chamber .

To meet the requirements of Clean Air Act , an efficient off gas cleaning system is necessary . The off gas is cooled down to 200 C by mixing with fresh air before it passes the cyclone separator . Thereafter , it is filtrated by using the filter group which consists of a self cleaning bag

and high efficiency particulate absolute (HEPA) filters . The purified gas is finally sucked by exhaust blower as it is emitted to environment via stack directly if no need for wet scrubbing system .

Ashes may be removed periodically from gas reactor , combustion chamber , cyclone separator , and bag filter into 40 litres steel drums with tight lid as it can be sent for stablization

3 . Waste Packages

The simulated MSW materials which comprise plastics , cellulose , and rubber shall be packed in a high quality paper bags of 5 litres capacity .

4 . Charging of Waste

The feed to the gas reactor will be conducted via a suitable ventilated glove box , as ventilation inside the glove box will be controlled in accordance with the relative pressure levels in the outside area and inside the gas reactor .

5 . Combustion Control

The heat required for initiating and controlling combustion in the gas reactor is mainly provided by using a burnt piece of wood or other similar materials and controlling the injected air , while combustion is provided inside the

combustion chamber by using burner fed with a commercial LPG during only start up. The burner is serving to bring the gas reactor and combustion chamber to the required thermal balance.

6 . Process Chemistry

Controlled air incineration is a simple process , being gasification of waste material is essentially a 1-step endothermic process as chemical compounds that form part of waste are gasified to form ultimately simple gaseous products.The gasification efficiency is quite dependent on :

- The operating temperature
- Quantity of air injected to the system
- Partial pressures of gaseous products

Some examples of the chemical reactions occurring with substances are as follow :

$$1/n\ (\ C_6H_{10}O_5\ )_n + 1/2\ O_2 = 6\ CO + 5\ H_2$$

$$1/n\ (\ CH_2\text{-}\ CH_2\ )_n + O_2 = 2\ CO + 2\ H_2$$

$$1/n\ (\ C_5H_8\ )_n + 5/2\ O_2 = 5\ CO + 4\ H_2$$

Unfortunately , the reactions cited are idealized .In reality ,organic waste are mainly producing high boiling organic products and elemental carbon .

To provide energy necessary for decomposition , group of exothermic reactions important to the system has to be secured as follow :

$$CO + 1/2\ O_2 = CO_2$$

$$H_2 + 1/2\ O_2 = H_2O$$

7. Off- gas treatment

In reducing waste volumes and destroying potentially municipal solid waste by controlled incineration process, air pollutants such as carbon mono oxide CO , sulpher oxides SOx ,nitrogen oxides NOx, and non combustible trace metal oxides(especially mercury,lead,and others) are potentially emitted with fly ashes and aerosols.

Because of the considerable concern about formation of such micro pollutants,the incineration trial runs have to be conducted utilizing the most modern and efficient techniques of off gas treatment.

In our case,LAWI is equipped with triple acting flue gas purification system separating solid particles, ash , dust,and aerosols from flue gas as follow :

-coarse separation :cyclone separator

-fine separation :bag filters

-ultrafine separation :HEPA filter

as more than 95 % of the particulate contained in the flue gas are retained in the bag filter,as aerosols are extracted from flue gas with efficiency of 99.97% in the HEPA filters.

The polluntant such as HCl and SO2 will be retained using wet scrubbing.In case of having very low chloride content,

wet scrubbing may be cancelled.

Table 1 shows the limits of heavy elements, and gaseous constituents in off gas emitted to the environment.

8. Process Control, Instrumentation ,and Safety Systems

The control for the various electromechanical components of the incinerator (exhaust blower,control valves,air blower,and burner) will be located on the control panel close to the installation.This panel will also contain the indicators for the various instruments measuring the temperature of the gas reactor,combustion chamber,and mixing cooler.

Pressures at different points and differential pressure for controlling the clogging of the bag filter,HEPA filters will be indicated by manometers (please refer to Fig.3 which represents P&I diagram)

The control of the incinerationplant will be carried out by five types :

I . Alarm with action

II Alarm only

III Indicators

IV Chart recorders

V Data acquisition system

as all alarms will be indicated by red LED s in the flow

sheet diagram on the control panel and additionally by lamps in combination with acustic signals.

Table 2 summerizes some examples of control with the subsequent built-in corrective actions.

9 .Quality and Yield Rate Product

The performance and experimental results obtained from processing the feedstock, containing mainly cellulosic materials,and plastic are descibed below.The following operational conditions were used :

Feed rate	: 15 Kg/hr
Gasification temperature	: 600-800 C
Combustion Chamber temperature	: 1000-1100
Average thermal power	: 70 KWH
Air consumption in gas reactor	: 10 Nm/hr
Total air consumption	: 1200 Nm/hr
Produced gas in gas reactor	: 51 Nm/hr
Flue gas temp. after mixing chamber	: 200 C

9.1 Composition of Gas Reactor Product Gas

Table 3 shows the composition of gas reactor product gas.The calorific value of produced gas was found approximitaley 1350 Kcal /m 3

9.2 Environmental Effects

The volume of exhaust gases from this demonstration plant is less than of that of the conventional incinerator for the same scale and the potentially harmful components contained in the exhaust gas are substantially lower than the values specified as standard for incinerator exhaust gas in Germany.Thus it was ascertained that this system is essentially pollution free.

1. Exhaust Gas

It was confirmed that the concentration of HCl,NOx,SOx and dust were found less than the values specified as the standards for incinerator exhaust gas(see Table 4)

2. Residues

It was found that ash has chemical and size uniformity which allow it to be stabilized and conditioned by any of accepted and proven techniques.

3. Others

It was proven that noises, vibrations ,offensive odors,were well less than the standard of the control regulations.

Conclusion

A summary of aforementioned brings about the specified conclusions :

- Low active waste incinerator with the latest modified design is proven as a powerful controlled facility for

a complete combustion,high destruction and removal efficiency,and maximum volume reduction factors are guaranteed.

-Cooling down of flue gases by admixing fresh air is simple method although it results in relatively big flow volumes.

-Minimization of harmful emissions such as NOx ,SOx ,CO to environment are secured.

- The dust and ashes loading of flue gas is kept as low as possible.

-The preliminary results revealed the necessity for the modification of feeding system to suit a wide range variety of municipal solid waste .

Table 1. Off Gas Composition Limits

Harmful gas/Heavy elements	New Clean Air Requirement
CO	100 mg / N m3
NOx	100 mg / N m3
CH4	20 mg / N m3
SOx	100 mg / N m3
HCl	50 mg / N m3
HF	2 mg / N m3
Particulate	0.6 lb / hr
Lead	1.5 u g / m3
Mercury	3.2 kg / day

Table 2. Examples of Controll and Safety Systems of LAWI

Description	Symbol	Alarm	Indication	Corrective Action
-Temp. of glowing bed	1 T 2	1 T 2-h1 1 T 2-h2	Temp. indicator Temp. indicator	Close valve 2MV4
Temp. of combustion chamber	1 T 4 a	1 T 4 a-l 1 T 4 a-h	Temp.indicator Temp. indicator	Switch on burner 4IB1 Switch off burner 4IB1
Temp. of the flue gas in mixing chamber	1 T 5	1 T 5-h	Temp. indicator	Switch off burner 4IB1 Open valve 2MV2
Pressure of produced gas after gas reactor	1 P 2a	1 P 2a-h	Manometer	Open valve 1MV1
pressure drop across glowing bed	1 Pd 1	1 Pd 1-h	Manometer	Supporting arm in glow bed will be rotated
Differential pressure across bag filter	1 Pd 2	1 Pd 2-h	Manometer	bag filters must be cleaned by compressed air
Differential pressure across HEPA filters	1 Pd 3	1 Pd 3-h	Manometer	HEPA filters shall be changed
Lack of feed	1 N 1	1 N 1-l	-	Add feed in a glove box

Table 3. Gas Reactor Product Gas Composition

Component	Composition,%
H2	26.1
O2	0.0
CO	15.3
CO2	7.1
H2O	13.1
N2	38.4

Table 4 . EXhaust Gas Composition

Component	Composition
O2	11 - 17 %
CO	35 ppm max.
CO2	2.4 - 4 %
NOx	10 ppm max.
SOx	25 ppm max.
Dioxines (PCDD)	Not detected
Furans	Not detected

L A W I

Low Active Waste Incinerator

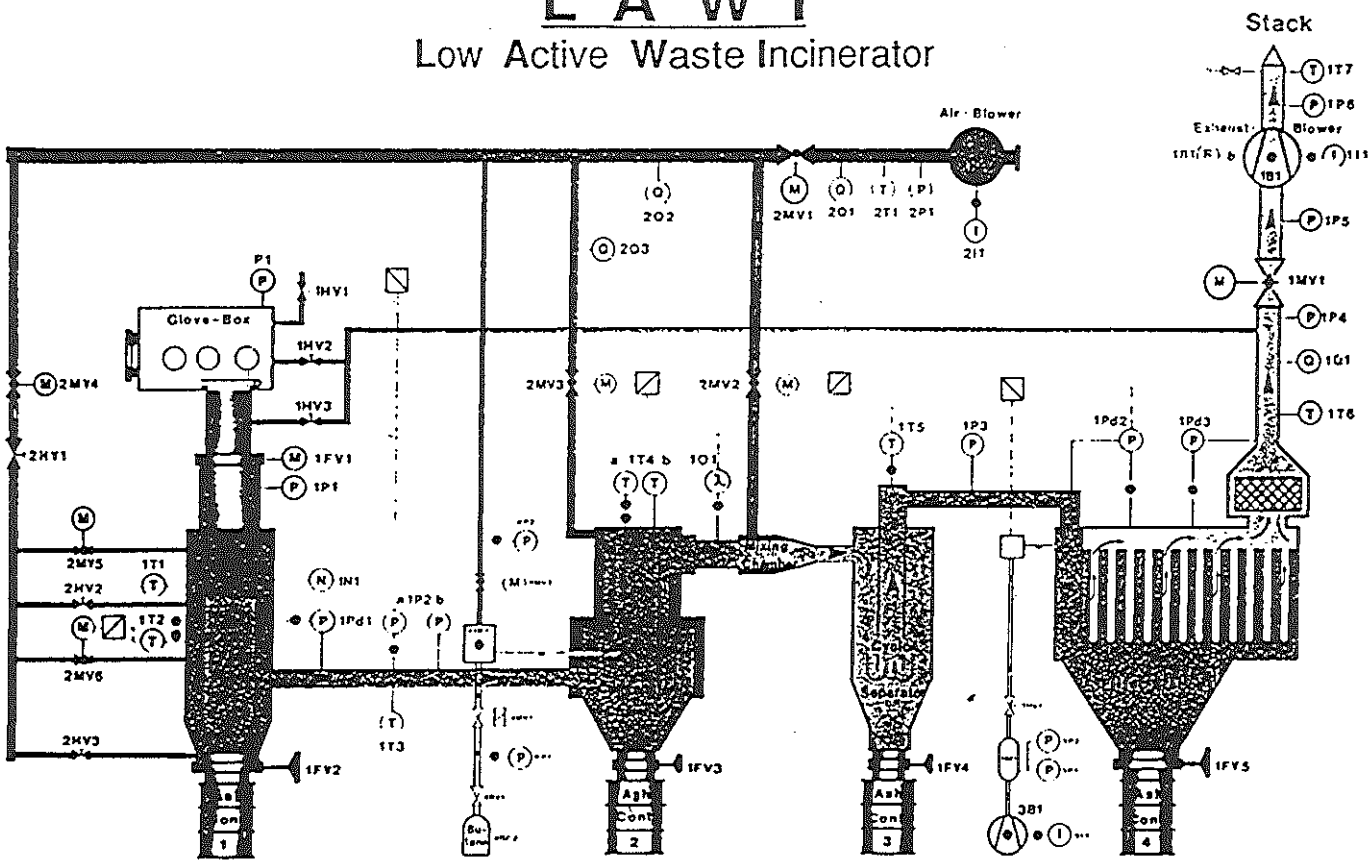
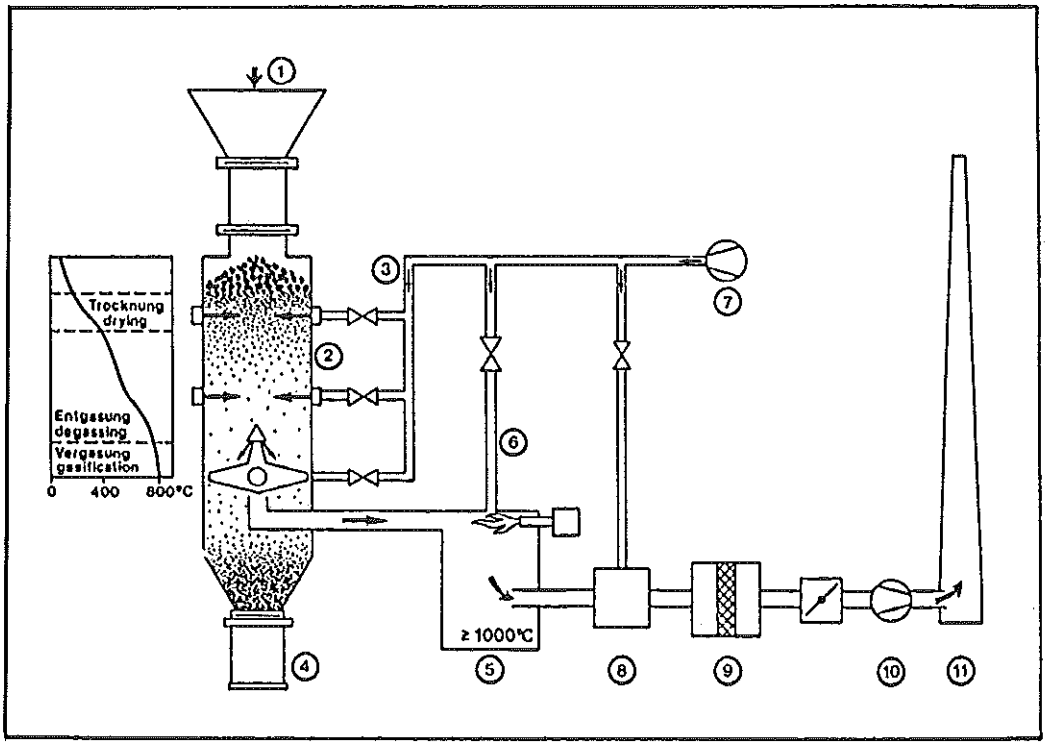


Fig. 2 LAWI Flow Sheet



1 Material feed
2 Gas Reactor
3 Gasification Air
4 Ash Discharge
5 Combustion Chamber
6 Comcustion Air
7 Air Supply
8 Off-gas Cooling or Heat Utilization
9 Off-gas Cleaning
10 Off-gas Release
11 Stack

Fig. 2 -The Jülich Thermoprocess, Operating Principle

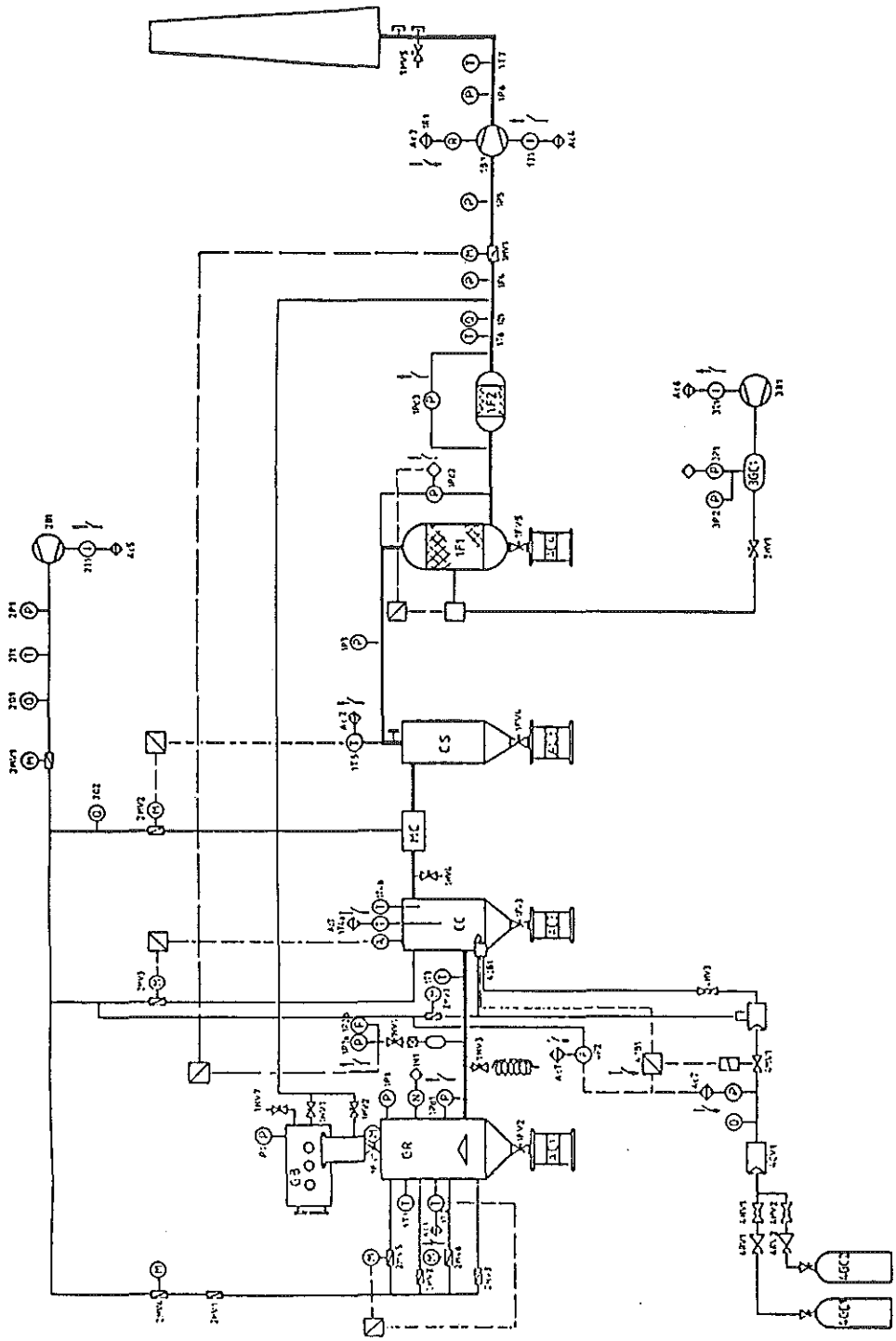


Fig.3 P&I diagram

Treatment of Industrial Waste effluents by Pyrolysis Residue

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b. Kernforschungszentrum Jülich, GmbH. IPC, Germany.

Abstract : The physicochemical nature of the adsorbent " pyrolysis residue " , " P.r ", used in this study was characterized in details. The extent of utilization of the full surface area of P.r. for adsorption of solute in single-component system and in binary-system is descirbed . Adsorption isotherms on P.r. for anthracene; phenanthrene; pyrene ; phenol ; o-,m-,p- cresol; 2,3,6- trichlorophenol; 2,4,6- trichlorophenol and pentachlorophenol have been determined. The data conform to the Langmuir adsorption isotherm. As well as, the competitive adsorption of organic solutes for the available sites on the P.r. surface is described. Also, the P.r. was examined for metals removal . In this concern, Cd, Zn, Pb, Cu and Ni are used . Finally, some applications for treatment waste water samples using P.r. are described in both batch and continuous- column tests.

A general practice for domestic waste treatment is incineration in an inert atmosphere at temperature around 800°C to produce gases, liquids and a charred residue called "**PYROLYSIS RESIDUE, P.r**". This waste treatment technology aimed into three goals: i. energy; ii. waste reduction and iii. recycling of raw materials. The P.r obtained from this process is generally collected and used as landfill. This research aimed to assess the possible use of P.r for industrial waste treatment. In this concern, the following aspects of P.r were investigated: a- characterization of the P.r; b- Response of typical pollutants to the P.r; c- Factors affecting sorption of different pollutants to the P.r; d- Applications for the use of P.r for industrial waste effluents treatment.

characterization of The P.r:-

The P.r supplied from (PYROLYSE-KRAFT-ANLAGEN) PKA- Germany was characterized in terms of chemical composition, structure, surface area, surface charge and sorption properties in solution. The following properties were obtained:

- P.r is a mixture of many chemical components (oxides, sulfides, ...etc) with 34.1% carbon and 54.7% ash.
- x- ray powder diffraction pattern indicates that the P.r is a mixture of two phases: Ca (Fe,Ca,Mn) Si_2O_6 & Pb_8 Sr $(SiO_7)_3$
- P.r contains micro- and intermediate as well as macropores, and it has a surface area of 42 m^2/g.
- P.r has zero charge at pH = 6.1 and can be used as a sorbent material from aqueous solutions.

SORPTION BY P.r:-

Sorption of selected organic and inorganic pollutants by P.r was investigated. Organic pollutants include: phenol, 2,3,6 -TCP, 2,4,6-TCP, PCP, o-cresol, m-cresol, p-cresol, anthracene, phenanthrene and pyrene. In table (1), the adsorbability of these organic compounds are given in terms of μg of solute removed from solution per unit weight of P.r as well as percent reduction of each solute.

TABLE(1): ADSORBABILITY OF THE USED ORGANIC COMPOUNDS TO THE PYROLYSIS RESIDUE

COMPOUNDS	SOLUBILITY in 100 parts H_2O *	CONCENTRATION mg/35 ml of solute initial (C_o)	final (C_f)	ADSORBABILITY μg/g	% red.
a. phenol	6.7	60	14.5	1594	76
2,3,6-TCP.	v.s.sl.	60	29.5	1069	51
2,4,6-TCP.	v.s.sl.	60	29.6	1064	51
PCP	0.008	60	22.46	657	31.5
b. o-cresol	3.1	60	50.56	330	16
m-cresol	2.5	60	48.27	411	20
p-cresol	2.3	60	46.02	489	23
	in g/l **				
c. anthracene	89×10^{-6}	30	22.34	894	26
phenanthrene	27×10^{-4}	30	19.12	1269	36
pyrene	20×10^{-5}	30	21.29	1016	29

* From reference (90)
** From reference (91)

NOTE:-(1) In preparation, the water/methanol ratio used as follows:

H_2O ml	:	CH_3OH ml	
750	:	250	(a,b)
600	:	400	(C)

(2)- 2,3,6-TCP = 2,3,6-trichlorophenol
2,4,6-TCP = 2,4,6-trichlorophenol
PCP = pentachlorophenol.

From these results, the following trends are documented. **Phenol and chlorinated phenols;** the polarity of these pollutants increases in the order:

pentachlorophenol > trichlorophenol > phenol.

In turn adsorbability decreases in the order :

pentachlorophenol < trichlorophenol < phenol.

The data also indicate that the position of substituents have a slight effect on adsorbability. Thus, the adsorptive capacity for 2,3,6-trichlorophenol and 2,4,6-trichlorophenol are nearly the same.

Cresols; solubility of cresols in H_2O is higher than pentachlorophenol and adsorbability is expected to be lower. Therefore, The difference in uptake percent is due to the difference in their solubility in water.

Polycyclic aromatic hydrocarbons; isomers didn't follow any particular pattern in the adsorption, which is confirmed by anthracene and phenanthrene. Pyrene is more spherical than phenanthrene i.e., pyrene has less surface area for interaction with the P.r surface and thus pyrene is less adsorbed than phenanthrene.

For inorganic pollutants, table (2), lists mg of sorbate removed per gram of P.r for some heavy metals, Cu, Cd, Zn, Ni and Pb. The percent reduction of these heavy metals due to adsorption is also given.

TABLE(2): SUMMARY OF TREATMENT RESULTS

METAL	TAKEN AS	pH	ADSORBABILITY red,%	uptake,mg/g
COPPER	$CuCl_2 .2 H_2O$	6	95	55
		7	98	57
CADMIUM	$3 CdSO_4.8 H_2O$	6	50	48
		7	47	45
ZINC	$Zn SO_4 .7 H_2O$	6	23	30
		7	45	58
NICKEL *	$NiCl_2 .6 H_2O$	6	--	--
		7	--	--
LEAD	$(CH_3 COO)_2Pb.3H_2O$	6	95	156
		7	96	157

* The initial concentration was 28 mg/l, the final concentration was 42.7 mg/l at pH = 6 and 41 mg/l at pH = 7.

From this table, it is clear that the % reduction of Cu and Pb ions are nearly the same. Cd ions were found to be adsorbed more than Zn ions and Ni ions didn't sorbed at all.

ADSORPTION ISOTHERMS:-

Adsorption isotherms for single and two component systems were carried out. For single component system, the isotherms are related to the Langmuir model. The following linear form is used:

$$\frac{C}{q_e} = \frac{1}{b\,Q^\circ} + \frac{C}{Q^\circ}$$

where,

C is the measured concentration in solution at equilibrium.

Q° is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface,

q_e is the number of moles of solute adsorbed per unit weight at concentration C.

b is a constant related to the energy or net enthalpy, ΔH, of adsorption, ($b \alpha e^{-\Delta H/RT}$).

Figure (1) is an example of the results for the linear relation obtained for adsorption of phenanthrene. From this relation Langmuir coefficients b and Q° are obtained.

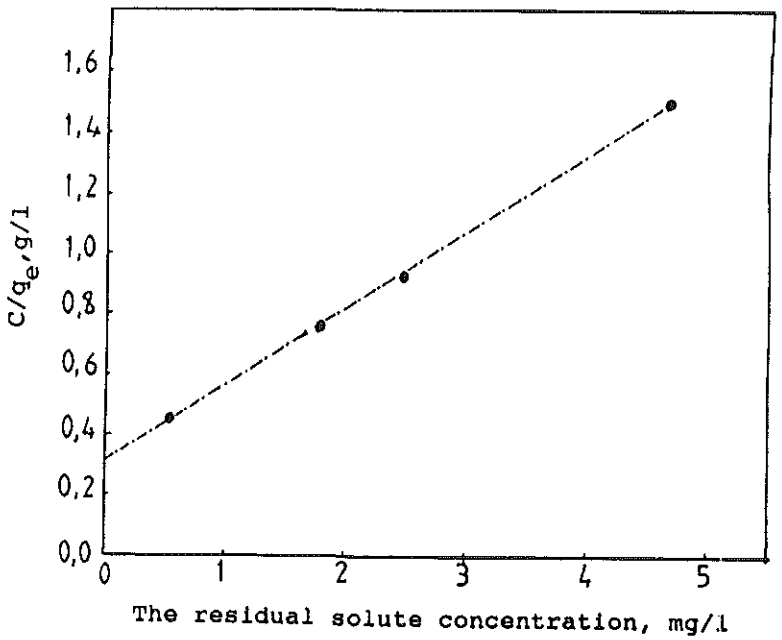

Fig.(1): : Adsorption of phenanthrene by the pyrolysis residue. (Linearized Langmuirian Relationship)

In table (3), the Langmuirian coefficients b $(mg/l)^{-1}$ and $q^{\circ}(mg/g)$ for substrates under investigations, both on weight and molar basis, are given.

TABLE(3): LANGMUIRIAN COEFFICIENTS FOR ADSORPTION OF INVESTIGATED ORGANIC COMPOUNDS ON PYROLYSIS RESIDUE

SUBSTRATE	M.W	$(mg/l)^{-1}$ b	(mg/g) q°	$(mmol/l)^{-1}$ b	(mmol/g) q°
Phenol	94.0	$3.40x10^{-4}$	833	0.032	8.86
2,3,6-TCP	197.46	$8.69x10^{-4}$	470	0.172	2.38
2,4,6-TCP	197.46	$3.29x10^{-3}$	467	0.649	2.36
PCP	266.35	$4.39x10^{-3}$	130	1.169	0.488
o-cresol	108.13	$1.08x10^{-2}$	80	1.17	0.739
m-cresol	108.13	$9.15x10^{-3}$	84	0.989	0.777
p-cresol	108.13	$7.55x10^{-3}$	86	0.816	0.791
Anthracene	178.22	0.912	0.022	163	$1.2x10^{-4}$
Phenanthrene	178.22	0.788	3.97	140	0.022
Pyrene	202.24	0.127	0.629	25.7	$3.1x10^{-3}$

NOTE: 2,3,6-TCP = 2,3,6-trichlorophenol.
2,4,6-TCP = 2,4,6-trichlorophenol.
PCP = pentachlorophenol.

For two component mixture isotherms, the Langmuir competitive model which permits calculation of $(q_e)_i$, the amount of species i adsorbed per unit weight of adsorbent in the presence of another adsorbing species J, was applied using the following relation;

$$q_{e,i} = \frac{Q_i^{\circ} b_i C_i}{1 + \sum_{j=1}^{n} b_j C_j}$$

Figures (2) and (3) describe adsorption of 2,3,6-trichlorophenol in the presence of 2,4,6-trichlorophenol by using Langmuir Competitive model.

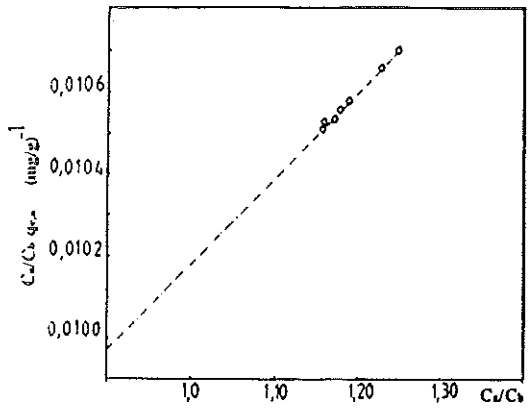

Fig (2): Adsorption of 2,3,6 - trichlorophenol in two - component mixture using the Langmuir Competitive Model.

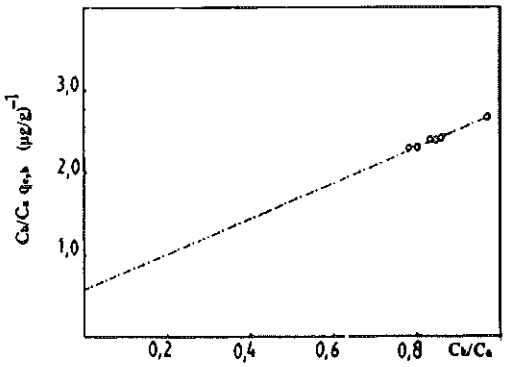

Fig (3): Adsorption of 2,4,6 - trichlorophenol in two - component mixture using the Langmuir Competitive Model.

Competitive adsorption between 10 organic compounds for the available sites on the P.r surface was studied. In this concern, the kinetics and equilibria of adsorption of o-, m-, p- cresols from a pure solution and from the mixture on the P.r surface are demonstrated, fig.(4). It is clear that there is a great reduction in the adsorption capacity of each solute in multi-solute system than that obtained in single solute system.

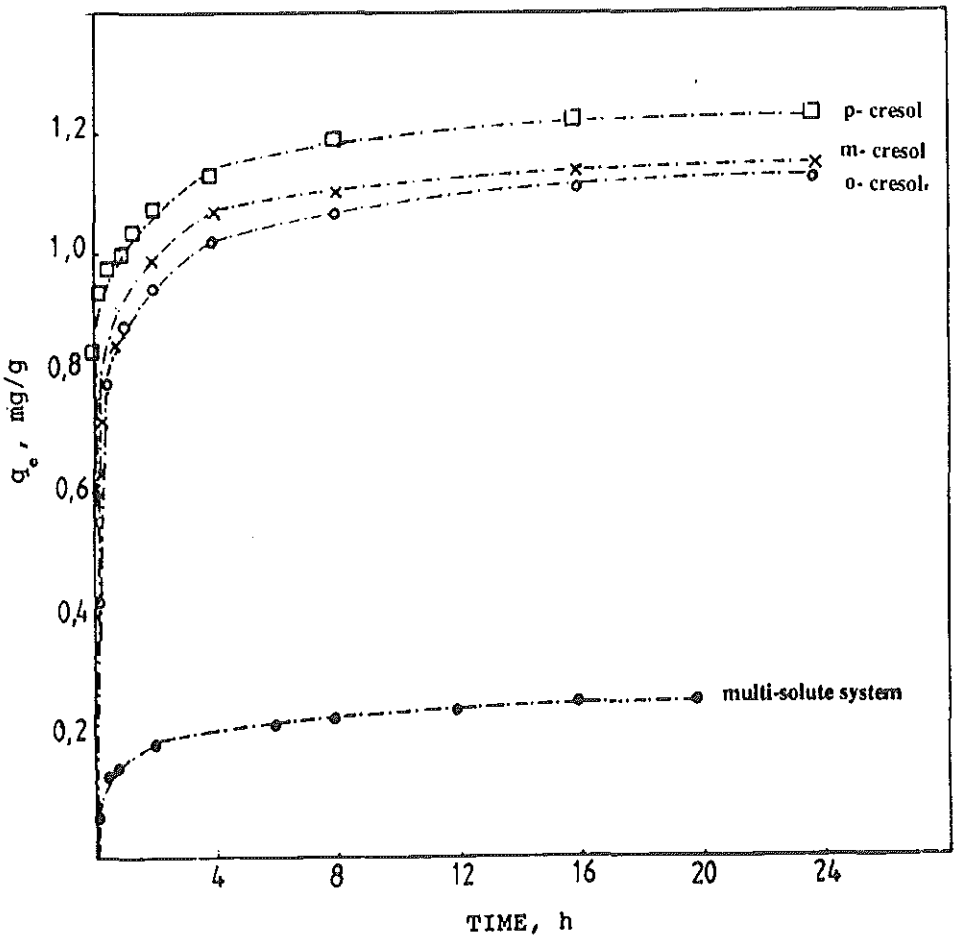

Fig.(4): Kinetic studies on the adsorption of o-,m-, and p-cresols from the pure solution and the mixture by the P.r.

Comparison between single component system and binary system should be constructive. in case of single component system, the monolayer capacity q°= 470 mg/g for 2,3,6-trichlorophenol

and q°= 467 mg/g for 2,4,6-trichlorophenol.

In case of two component system;

$$q^{\circ}(2,3,6\text{-TCP} + 2,4,6\text{-TCP}) = 112 + 357 = 469 \text{ mg/g}.$$

This finding indicates that the amount of 2,4,6-TCP on the P.r surface is more than three folds that of 2,3,6-TCP. This is due to the difference in the affinity of each solute on the P.r surface as given by the value of (b).

APPLICATIONS:-

In this section, possible treatment of industrial waste by P.r was assessed. In this concern, both batch and column investigations were carried out.

Assessment of the treatment process was in terms of measuring the chemical oxygen demand (COD) before and after treatment as a measure for organic contaminants. The sample treated was obtained by PKA, Germany. The samples are obtained by washing the exhausted gases during the carbonization process.

THE MODES OF OPERATION:-

1. BATCH SYSTEM:-

The efficiency of the P.r on the reduction of COD is illustrated graphically in figures (5, 6). In fig. (5), it is clear that as the P.r dose increases, the amount of the COD removed, also, increases. i.e, the variation is linear.

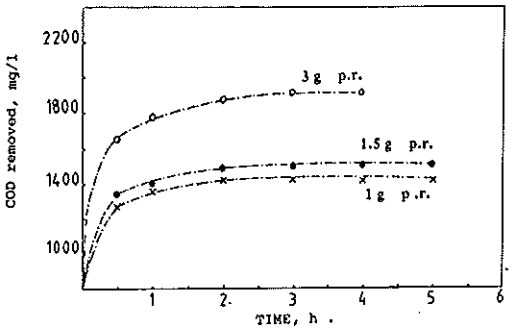

Fig.(5): Efficiency of the pyrolysis residue on the removal of COD (P.r. effect).

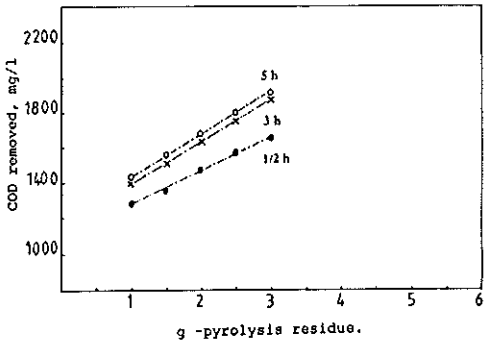

Fig.(6): Efficiency of the pyrolysis residue on the removal of COD (time effect).

The data represented in fig. (6), shows a gradual increases in the COD amount removed by the P.r as the shaking time increases. Also, it can be seen that the P.r has a considerable influence on the removal of the COD, but the efficiency is less than that of the activated carbon (R-444). cf.table (4).

TABLE (4): COMPARISON BETWEEN THE ACTIVATED CARBON AND THE P.r ON THE REMOVAL OF THE COD

INITIAL COD mg/l	ACTIVATED CARBON (R-444)	PYROLYSIS RESIDUE
2109	658	1642
2120	668	1649
2102	647	1630

The effect of uv -irradiation in absence and presence of H_2O_2 was investigated. From table (5), it was clear that uv-irradiation has a significant influence on removal of COD. Taking into account that uv-exposure time has no significant influence, cf.table (6).

TABLE (5): EFFECT OF UV-IRRADIATION IN PRESENCE AND ABSENCE OF H_2O_2 AND THE P.r ON THE REMOVAL OF THE COD.

CONDITIONS	INITIAL COD mg/l	COD, mg/l		REMARKS
		Before UV	After* UV	
In absence of H_2O_2	1966	701	631	pale yellow
In presence of H_2O_2				
1 ml	1966	725	641	colourless
5 ml	2109	849	665	colourless
10 ml	2326	762	536	colourless

•EXPOSURE TIME OF ONE HOUR FOR ALL MEASUREMENTS.

TABLE (6): EFFECT OF UV-EXPOSURE TIME ON THE REMOVAL OF THE COD

UV-EXPOSURE TIME, h	COD mg/l
1	633
2	631
3	634
4	636

Moreover, a significant loss in the COD was obtained in presence of a high volume of H_2O_2. The data in table (7) shows that the excess of H_2O_2 than 12.5% of the waste water volume causes adverse effect on the removal of the COD of the filtrate.

TABLE (7): EFFECT OF H_2O_2 AMOUNT ON THE REMOVAL OF THE COD

H_2O_2, ml	COD, mg/l
--	2326
5	600
10	532
20	484
40	782
60	980

Based on the aforementioned results, a recommended method is developed. In this concern, the following flowsheet is successful to fulfill the allowable level of COD ≈ 200 mg/l and thus the treated water will pass into rivers, cf. fig.(7).

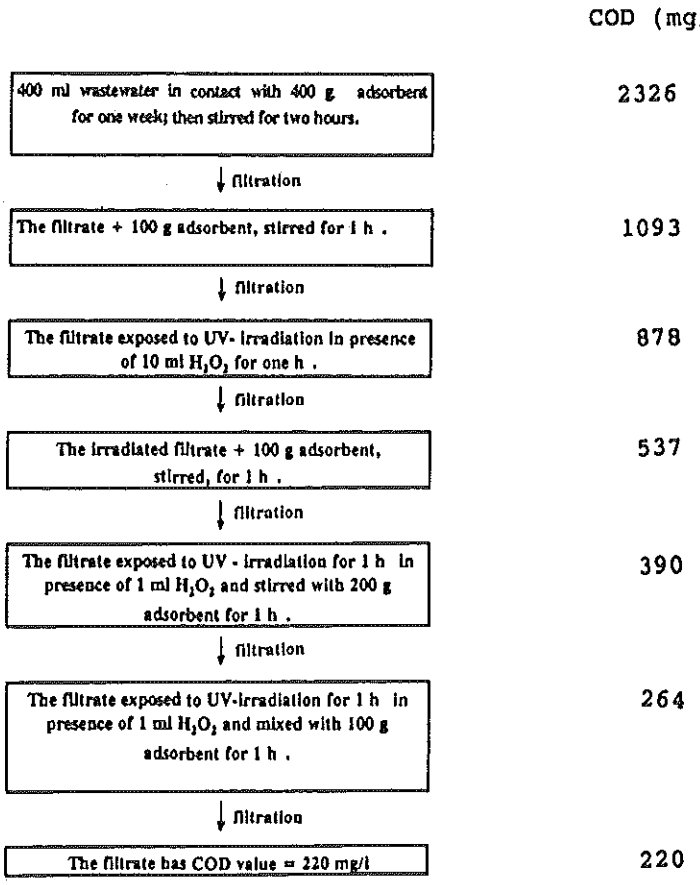

Fig.(7): flowsheet tested for treatment waste water samples.

2- CONTINUOUS-COLUMN TESTS:-

Figures (8, 9) illustrate the breakthrough curves of the waste water samples using the P.r as a sorbent material. In these graphs, the effluent COD in mg/l is represented on the ordinate and the effluent volume in ml is denoted on the abscissa.

The proper interpretation of small - scale continuous column tests is illustrated in figures (8, 9). The shape of the column exhaustion curves is significant and implies that there are many impurities to be removed due to the breakthrough curves are gradual i.e., the adsorption zone is likely to be deep. As a general rule, the time to the break point is decreased by increasing the flow rate of the effluent, decreasing the bed depth of the P.r in the column used and increasing the internal diameter of the column.

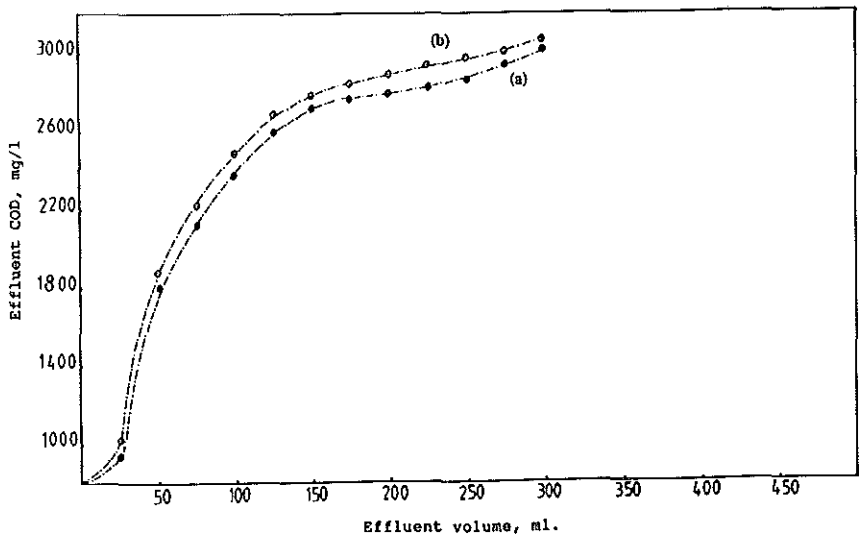

Fig.(8): Experimental breakthrough curves of the wastewater sample using the pyrolysis residue as a sorbent material.

a). I.D. = 2.1 cm; F.R. =2 ml / min.; and bed depth = 11.4 cm.
b). I.D. = 2.1 cm; F.R. =1 ml / min.; and bed depth = 11.4 cm.

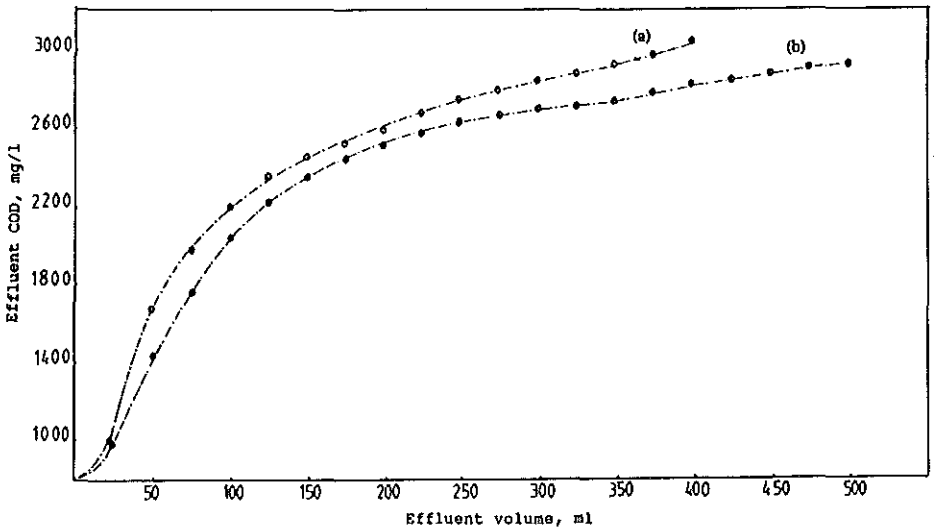

Fig.(9): Experimental breakthrough curves of the wastewater sample using the pyrolysis residue as a sorbent material.

a).I.D. = 3.3 cm; F.R = 1 ml / min; and bed depth = 4.8 cm.
b).I.D. = 3.3 cm; F.R = 1 ml / min; and bed depth = 9.6 cm.

GENERAL CONCLUSION

Treatment of waste water in batch systems using the P.r coupled with UV - irradiation in the presence of H_2O_2 is more promising than the solid bed.

* * * *

Finally, the loaded matrix of P.r can be used in construction of roads, making of concrete and cinder blocks and the treated water will pass into rivers and can be joined to the natural water treatment plans.

UPTAKE OF HEAVY METALS BY CROP PLANTS.

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1. Introduction

Agricultural interest in heavy metals bases on their toxicity. The majority of agricultural heavy metal research was therefore devoted to clarifying factors related to the transfer of metals from the soil to the food chain. In addition to food crops further interest is now growing in metal uptake and metabolism by non-food (industrial) crops. Industrial crops provide an alternative possibility for agricultural utilization of heavy metal polluted areas and a potential for their decontamination through "metal harvesting". Working out basic information on the behaviour of heavy metals in soil-plant systems is therefore a prerequisite for agricultural management of polluted soils.

2. Heavy metals in soils

Heavy metals are natural components of the earth crust (Tab. 1, Wedepohl 1991). Heavy metals included in the composition of the parent material may be set free in the course of weathering and soil formation. The further fate of the released heavy metals depends on many climatic and pedological factors as well as agronomic practices. Depending on these factors, some heavy metals may be leached out while other elements may accumulate in the top soil. In addition to this native origin, some heavy metals may be supplied to soils by atmospheric deposition and by agronomic practices such as fertilizer and pesticide application as well as the disposal of municipal wastes such as composts and sewage sludge on agricultural land (Cramer et al. 1981, Sauerbeck 1985, Schmidt and Sticher 1991).

Examples of heavy metals supplied to agricultural land through the application of sewage sludge are given in table 2. They indicate that the heavy metal (Cd, Cu, Hg, Pb, Zn) concentration of sewage sludge may exceed their soil concentration by a factor of 20 and more (Sauerbeck 1985). This means that the disposal of sewage sludge must result in a gradual accumulation of these metals in agricultural soils.

Another example of heavy metal pollution of soils through fertilizer application is illustrated by the cadmium content of rock phosphates. As indicated in table 3, the Cd content of rock

Table 1: Heavy metals of agronomic significance in the continental earth crust and in soil,mg/kg dry wt.

Elements	Earth crust[1]	Soils[2]
Cr	88	2 - 50
Co	19	1 - 10
Ni	45	2 - 50
Cu	35	1 - 20
Zn	69	3 - 50
Mo	1.5	0.2 - 5
Cd	0.1	0.01 - 1
Pb	15	0.1 - 20
Hg	0.02	0.01 - 1

[1] Wedepohl 1991, [2] Cramer et al. 1981

Table 2: Common heavy metal concentrations[1] in soils and sewage sludge, mg/kg dry wt.

Element	Sludge	Soil	Sludge/Soil ratio
Cr	400	50	8
CO	15	10	1.5
Ni	100	20	5
Cu	650	20	32
Zn	1500	50	30
Mo	6	2	3
Cd	20	0.5	40
Pb	400	2	20
Hg	5	0.03	167

[1] Sauerbeck 1985, modified.

phosphates may vary considerably within a range of 3 - 75 mg/kg. Assuming a fertilizer requirement of 20 kg P/ha the cadmium input may reach an amount of 10 g Cd/crop. The application of phosphorus fertilizers and sewage sludge may increase the Cd concentration in the top soil from a common level of about 0.1 mg/kg to several milligrams per kg and industrial pollution may raise the Cd content of soils by a factor of 10^3 and more (Chen 1991).

Table 3: Cadmium content of rock phosphate[1] and Cd input into soil.

Source	P_2O_5 %	Cd-content mg/kg	Cd-input[2] g/ha
Senegal	33	75	10.3
Togo	37	65	7.9
Tunis	33	30	4.1
Israel	32	23	3.2
Maroc	32	22	3.1
USA	33	8	1.1
Syria	31	8	1.2
South Africa	37	3	0.4

[1] Sauerbeck 1985, [2] Assuming a fertilizer rate of 20 kg P/ha.

3. Bioavailability of heavy metals in soil.

The uptake of heavy metals by plants depends on their concentration in soil. An example of this concentration dependence is illustrated in Fig. 1. The uptake of heavy metals from soil is, however, not a simple function of soil total heavy metal content. This is attributed to the fact that heavy metals in soil are bound to various soil constituents into chemical forms of differing solubility and plant availability (Sposito et al. 1982). Soil factors which govern the plant availability of heavy metals have been the subject of intensive research during the last years (Sauerbeck and Lübben 1991, Adriano 1991, Merian 1991). These investigations showed that the availability of heavy metals to plants depends on several soil characteristics which affect the binding and mobility of metals in soil. These include soil pH, ion exchange properties, drainage status as well as clay and organic matter content (Berrow and Burridge 1991, Sauerbeck and Lübben 1991).

On the other hand these investigations demonstrated clearly that the plant itself plays an active role towards mobilizing and uptake of metals bound in soil with considerable differences among plant species and cultivars (Helal et al. 1990, Hinsely et al. 1978, Mench et al. 1989, Pettersson 1977). This is not surprising since the genetic dependence of many plant characteristics and root activities which may affect heavy metal uptake is well known (Randall et al. 1993). Plant and soil factors related to heavy metal uptake are summarized in tab. 4. They indicate that plant characteristics and activities may affect heavy metal uptake in several ways. These include the modification of soil properties related to heavy metal availability, the control over heavy metal transfer across cell membranes, the binding of metals in various plant tissues and the interaction between the nutritional status of the plant as well as environmental stress conditions with these activities.

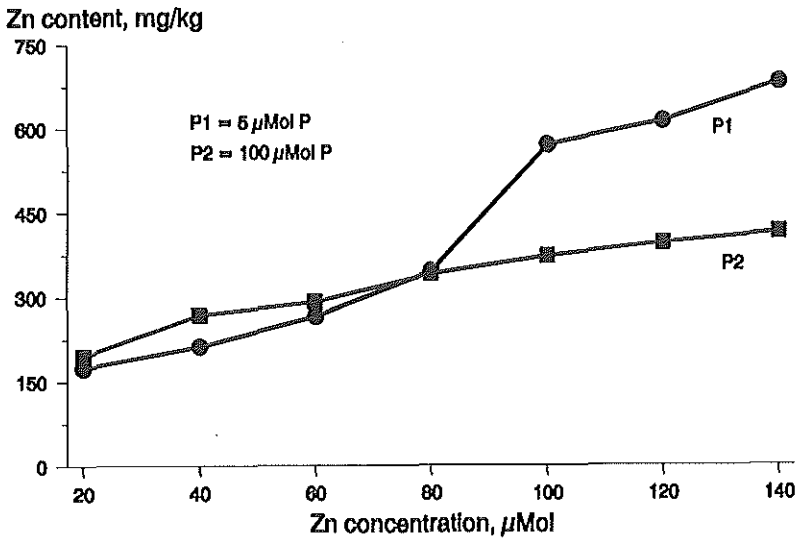

Figure 1: Zn content of spinach leaves as affected by Zn and P supply in solution culture.

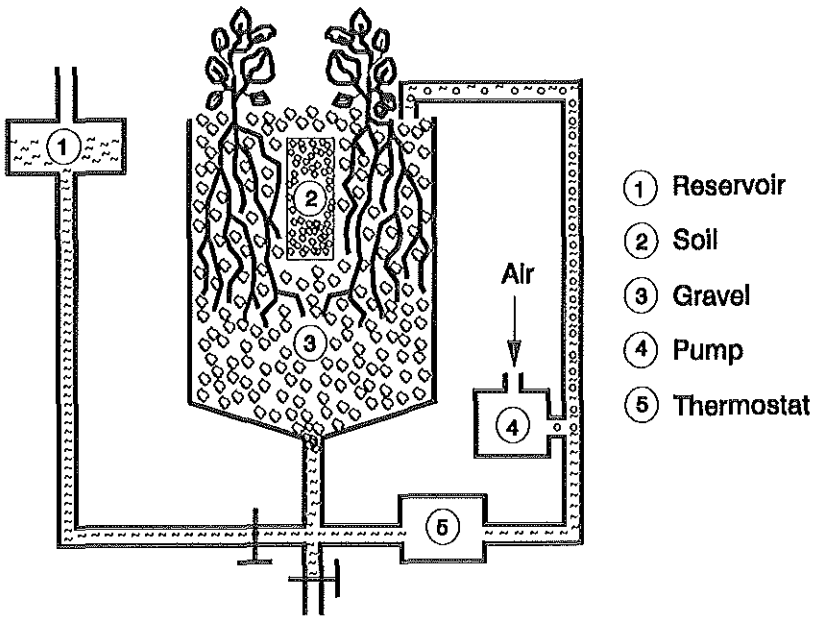

Figure 2: A circulating solution system for studying plant-root-soil interactions.

Table 4: Soil and plant factors related to heavy metal uptake.

Soil factors	Plant factors
Soil pH	Anion/cation balance
Organic matter	Root exudates
Clay content	Physiological stress
Cation exchange capacity	Metal binding
Soil strength	Membrane characteristics
Drainage status	Nutritional status

In the authors laboratory a special technique (Fig. 2) was developed for studying root-soil interactions (Helal). The main features of this technique is a flowing solution through a rooted gravel-soil substrate. This solution can be repeatedly and indestructively sampled for analysis of root exudates and solubilized nutrients and heavy metals. Results obtained with this technique showed that root exudates may raise the soluble organic carbon concentration in the rhizosphere with a corresponding increase in metal solubility (Helal 1990).

4. Transfer of heavy metals to the food chain.

Depending on the magnitude of heavy metal contamination as well as the many plant and soil factors which affect heavy metal uptake (summarized in table 4) and the differential behaviour of individual metals in soils and plants, various crops are expected to show considerable variation of heavy metal concentrations. An example of the variation of Cd concentration is indicated in table 5. It shows that the cadmium concentration of plants grown on non contaminated soils may be as low as 0.02 mg/kg and varies by a factor of 18. The data summarized in table 5 demonstrate furthermore that crop plants are able to accumulate Cd from polluted soils to reach concentrations of more than 160 mg/kg. This corresponds to an increase of Cd concentration by a factor of more than 3000.

Plant species differ not only in heavy metal uptake but also with respect to the translocation of metals to various plant organs (Klein et al. 1981, Sauerbeck and Lübben 1991). This differential translocation is of special significance for the transfer of heavy metals to the food chain. As indicated in table 6 for example Cd may be retained in the roots (beans). In most cases, however, Cd is translocated to the above ground plant parts. While old leaves often show the highest Cd concentrations, the transfer of Cd to the fruits and seeds is rather limited. Inspite of this restricted translocation to the fruits and seeds, table 6 demonstrate that even a relatively low level of soil Cd pollution (1.4 mg/kg) is often sufficient to raise the plant Cd content beyond the recommended limits for food contamination (table 7).

Table 5: Cadmium concentrations in plants[1], mg/kg.

Plant species	Nonpolluted soils	Polluted soils	Enrichment ratio
Wheat	0.05	12	240
Flax	0.11	32	290
Rapeseed	0.31	38	123
Maize	0.10	63	630
Tomato	0.02	80	4000
Spinach	0.11	160	1455
Tobacco	0.40	164	410

[1]Whole plant analysis in different experiments, partially under severe pollution.

Table 6: Distribution of Cd among plant organs as dependent on soil Cd concentration[1]

Plant species	Plant part	Soil Cd, mg/kg 1.4	4	10	30
Carrot	leaves	1.1	7.2	12	16
	beet	0.9	4.6	8.2	14
	roots	0.8	12	15	35
Salad	old leaves	1.1	9.6	26	44
	young leaves	0.9	3.8	8.1	18
	roots	0.9	4.2	11	21
Tomato	leaves	2.7	14	30	33
	fruit	0.4	1.2	1.6	2.4
	roots	1.0	5.3	9.2	18
Beans	leaves	0.2	0.4	0.5	0.9
	seeds	0.2	0.2	0.2	0.2
	roots	0.9	2.8	8.2	14
Maize	leaves	0.9	5	21	26
	grain	0.5	0.6	0.7	0.8
	roots	0.7	2.1	4.3	9.3

[1]Klein et al. 1981

Table 7: Recommended limits for heavy metal concentration in food[1], mg/kg fresh wt.

Food		Lead	Cadmium	Mercury
Vegetables	(leaves)	1.2	0.1	
Vegetables	(fruit)	0.2	0.1	
Vegetables	(roots)	0.5	0.05	
Stone fruits		0.5	0.05	
Cereal grain crops		0.5	0.1	0.03
Potato		0.2	0.1	0.02

[1]Bundesgesundheitsamt (Federal Bureau of Health) 1979

5. Concepts for soil remediation.

The development of concepts and measures for the amelioration of heavy metal polluted areas must take two aspects into account:

1. heavy metals are firmly bound to soil constituents and therefore cannot be removed from soil by simple leaching techniques,
2. due to continuous inputs e.g. through atmospheric deposition, the application of agrochemicals and waste disposal, the heavy metal content of soils may tend to increase with time.

Concepts for soil amelioration may be divided into two contrasting groups:

1. reduction of plant availability, and
2. removal of heavy metals from soils.

The simplest way to reduce the bioavailability of heavy metals in acid soils is to raise soil pH by the application of lime (Sauerbeck and Lübben 1991). The amelioration of neutral soils is, however, rather difficult. Certain soils additives such as FeS (K. Navabi, Institute of Soil Biology, Braunschweig, personal communication) may achieve some success. Little is known, however, about the effect of such additives on the plant availability of micro nutrients and on soil fertility in general.

The removal of heavy metals from soils may be achieved by either technical (extraction) or biological (harvesting) methods. An example of technical amelioration of metal polluted soils is the so called "electrokinetic remediation" (Acar and Alshawabkeh 1993). This method uses low level direct current of the order of mA/cm^2. Extraction and removal of metals may be accomplished by ion exchange at the electrodes or in an external extraction system. In the absence of reliable information on the efficiency and economics of this method, it is not possible to evaluate its applicability to agricultural soils.

Table 8 Potential annual Cd harvesting (kg Cd/ha) as dependent on biomass production and Cd concentration.

Cd tolerance	Cd concentration	Yield, 10^3 kg/ha		
	mg/kg	5	10	20
low	10	0.05	0.1	0.2
medium	50	0.25	0.5	1.0
high	100	0.5	1.0	2.0

The potential for the use of metal accumulating plants for decontamination of metal polluted soils was discussed by Baker et al. 1992. Shortcomings of this concept are related to the expensive production of plant material of no economic value and the disposal of contaminated plants. In contrast to short term decontamination techniques, the production of non food crops on contaminated soils seems to provide a feasible long term utilization/remediation possibility for polluted soils. Metal harvesting by the crop will depend on not only on its metal accumulation efficiency but also on its tolerance i.e. on its ability to maintain adequate growth rate (biomass production) under conditions of high metal availability.
The examples presented in table 8 cover a range of Cd accumulation and tolerance levels. According to these values more than 200 croppings are needed to remove 100 kg Cd from the top soil by a crop of medium tolerance and yield potential.

Acknowledgement:
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6. Literature

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Analytical methods used in determining trace elements in environmental matter*

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Abstract:

A survey on the performance of different methods and on the stategies in trace element analysis is given, starting with some remarks on abundance and relevance of element traces in the environment. Improvements in micro- and trace analysis are in progress. The aims of this progress are identified. A comparison of the power of detection of analytical methods is presented. Comments are made on some recent improvements in atomic spectroscopy and in probe methods. The importance of accurate data is exemplified, considering mercury in the environment world-wide. The pathway to accuracy is labourious and expensive. The respective strategy is outlined. The benefit is briefly considered that nuclear methods contribute to that strategy.

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1. Introduction

Analytical chemistry is being more and more involved, in a central position, into collaborative approaches together with various disciplines. This appears, whereever questions have to be answered that are related to the chemical composition of matter, the purity of matter and the uniformity of matter. Questions arise from the fast development of modern technology and modern society, which are highly relevant to secure and to protect the quality of life. Analytical chemistry is challenged here to contribute to the solution of many problems, but also to explain about the reliability of the analytical statements. Analytical science is steadily advancing into areas of local dimensions, trace concentrations, as well as levels of purity, that have not been accessible before [1-3]. Prominent areas posing those questions extend from biology, medicine, geochemistry, environmental science, to materials science and engineering.

2. Purity of matter versus omnipresence of elements

Apparently simple questions, however, may turn out to be difficult ones, considering the questions of purity, as e.g. the purity of water or of foodstuffs. Considering the matter in our environment from the point of view of elemental analysis we have to admit: A pure substance, in an absolute sense, which means completely free from any concomitant, does not exist at all! During the history of earth, elements have become enriched or diluted locally, but nowhere so that an element has been separated completely. There is no method of separation qualified to succed in complete 100% separation of two elements in macroscopic amounts. Instead, all elements are present in all matter, partly in extremely low concentrations of 10^{-12} to 10^{-15}. These concentrations of omnipresence are not yet known for all elements.

In the earth's crust, the elements are present in very different amounts and very different ubiquitous concentrations, according to their geochemical history. The more abundant elements are listed in Table 1 according to their fractional portion in magmatic rocks. Most of the prevailing 17 elements also constitute the main part of biomass: O, Fe, Ca, Na, K, Mg, H, P, F, S, C. These are represented in boldface in Table 1. Out of the abundant elements, only Si, Al, Ti, Mn, Ba, Sr are low in concentrations in organisms, down to the ng/g-range. As well known today, all other elements are ubiquitous in organisms, at concentration levels above the 0.1 ng/g-range for most elements. Only for very rare elements like the platinum group metals, no data have been established up to now.

3. Essentiality versus toxicity of trace elements

As is weel known, 16 trace elements are today identified, as being essential in our organism. However, if given concentration thresholds are exceeded, they can also produce negative effects on the living conditions of individuals or ecosystems. Each essential trace element exerts its vital function over a relatively narrow range of concentrations(see Fig. 1, from [4]). Too little leads to just as serious a problem as too much [5]. Optimal living conditions are sometimes restricted to only one order of magnitude. The most impressive example is selenium. Concentrations of selenium of more than 1 μg/g, taken up in the daily nutrition, lead to selenosis, so that level is toxic. On the other hand, selenium deficiency in nutrition, which is below 0.2 μg/g, causes severe damage to health. Such symptoma were first seen in Keshan in China. The important function of selenium is to fulfill encymatic effects, but it can further bind mercury to render it biologically inactive. Consequently, the analyst must be in a position to make an unequivocal distinction as to whether this "normal" (optimal) range is maintained, exceeded, or not reached [6].

4. Aims in micro- and trace element analysis

4.1. Accuracy of data on element traces

In this relation, it is interesting to see what the normal concentration range is for several trace elements in the widely studied biological matrix "human serum". In comparing "normal" data recorded in Fig. 2, a) in the period before 1976, b) after 1976 and c) today, the question arises: Why has this normal range been shifted to lower values for several trace elements during the last 20 years, and why has it stayed constant for others?

The answer is obviously connected with the reduction in systematic error of the determination of elements, primarily with the reduction of blank values from the analytical procedures. Elements that have been difficult to determine, at those levels, like Al, V, Cr, Mn, Co, Ni, Mo and Sn have been found substantially reduced, by a factor of 5 to 100. These are real problem elements at trace levels. The elements Cu, Zn and Se have been found in agreement with each other over these periods. Those determinations are unproblematical nowadays [4,7]. Radiotracer techniques [8] and nuclear activation analysis have contributed a lot to the improvement of those data. Blanks of analytical procedures have been drastically reduced by those means. Numerous fundamental studies have contributed to (a) detect errors also in the sampling procedures of biological materials, and (b) consequently to avoid them, utilizing radiotracers and activation

analysis. Surgical instruments made of plastics instead of steel, or from titanium, titania-ceramics, and fused silica for sampling of biological materials have clearly been a consequence of radiochemical fundamental studies. Those had identified superelevated levels of Co, Cr, Ni as having been caused by stainless steel instruments [7,9].

Improvements of micro- and trace-analysis (see Fig. 3, from [3]) are always pushed and motivated by the endeavour to optimize analytical economy, limits of detection, accuracy, local resolution and selectivity to different chemical species [3,10,11]. However, these characteristics are very closely interconnected and strongly interacting altogether. The stronger the power of detection, the finer the local resolution, and the higher the selectivity to different species of the same element is, the more expensive the analytical procedure tends to be. Similarly, the susceptibility to trouble and interference tends to increase.

Improving the reliability requires high expenditure in instrumentation and work load, thus directly reflecting onto economy. Finally, a procedure apparently designed to economic benefit will turn out to become completely ineconomical, if the accuracy cannot be guaranteed to meet the demand, and if wrong analytical data cause wrong action, either in medicine, or environment, or materials science [3,4,10].

4.2. Detection power

Looking first upon the direct methods for traces, we consider the power of detection of these methods in Fig.4 . Element concentrations have to be determined in all relevant matrices, including minerals, soils, sediments, sludges, water, air, plants, animal tissue and even protein fractions [4,10,13-15]. Such determinations must be accurate, down to concentration levels of the elemental omnipresence. Levels of omnipresence actually set the lower limit for trace determinations in environmental matter. Thus, a power of detection down to the ng/g-range is required, and even lower in cases where chemical species have to be differentiated.

X-ray spectrometry. X-ray fluorescence analysis XRF is used to determine elements of atomic numbers $Z > 11$ in solids and solutions. Light elements down to boron can also be detected, on principle, but they are not efficiently determined in solid matter of higher atomic number [16]. Particulate matter and slurries can be analyzed as a loosely poured bulk, as a pressure-compacted sample, or after isoformation by fusion in several flux

media. The detection limits are relatively high on the µg per g level. Calibration requires standard reference materials similar to the sample materials, to correct for matrix effects.

In comparison with the classical chemical principles and other modern methods [2,17], we state for environmental samples: Classical methods of titrimetry, spectral photometry, chelate-chromatography, ion-chromatography and voltammetry still keep a position in problem oriented analytical chemistry. Their detection power is good, and most of all, problems are small in calibrating them. In some cases, inverse voltammetry, particularly adsorption voltammetry, reaches limits of detection in the lower pg-region. However, those methods are usually applicable only for a few elements simultaneously, they require lots of time and of practical experience. These drawbacks from the economical point of view are overcome, in part, by combination with flow-injection procedures [18,19] or automation [20]. Limitations of the detection power are generally due to blanks and some other sources of systematic error, as e.g. adsorption, desorption, volatilization.

Recent improvements in atomic spectroscopy. Atomic spectrometric methods, including optical absorption, emission, and fluorescence offer determinations in the nanogram-range, in general, up to the picogram-range in favourable instances [21]. In atomic absorption spectrometry AAS, there are improvements realized by improved furnace techniques (coated tubes, platform technique), cold vapour (Hg) and hydride techniques (As, Se, Te, Sb). By applying physical and chemical methods (gas phase separation; electrochemical separation) of preconcentration, detection power at the femtogram-level can be reached. Absolute detection power of AAS can be improved one order of magnitude, by time resolved signal processing and signal averaging. Even more impressive, powerful improvements have been achieved by employment of lasers, more recently [22,23]. Cheap solid-state diode lasers have already been made the base of an atomic absorption instrument for the determination of the alcaline and earth-alcaline elements [23]. These lasers are easily tunable, so that different analytical lines can be selected. The laser emission lines are extremely narrow-banded, yielding very high dynamic ranges in element analysis. This can be achieved using instrumentation without monochromators. It is expected that also shorter wavelengths will be produced by diode lasers in the near future. Then, this will soon turn into a relatively cheap analytical technique [2,22,23].

Developments in optical emission spectrometry OES focus to problem-oriented

applications. A number of powerful sampling and excitation principles are at disposal, viz. high frequency and microwaves, laser-evaporation and cathodic ion sputtering. Detection power of inductively coupled high frequency plasma ICP-OES ranks between those of flame-AAS and electrothermal-AAS, comparable to direct current plasma DCP-OES and sparc-OES. Empirical studies showed that ICP-OES is less subject to interferences by alkaline elements as compared to DCP-OES [2].

The microwave induced plasma MIP-OES is a powerful micro-method for a number of elements (e.g. Fe, Co, Ni, Cu, Zn, Cd, Hg, Tl, Bi) with detection power at the picogram-level in solutions and gaseous phases. The MIP-OES has been successfully incorporated as a sensitive element-specific detector into on-line combinations with gas-chromatography and high performance liquid chromatography HPLC, particularly for element species analysis.

Current developments strive to improve the power of detection, but also to reduce the matrix-dependence, basically by means of de-coupling the individual steps of (1) sample evaporation, (2) atomization and (3) excitation. E.g., direct electrothermal evaporation was coupled to ICP-OES. The need for any compromises is avoided by this de-coupling, for the benefit of single-step optimization. A number of recent developments have yielded advancements into this direction [see, e.g. 2,12,21,24].
The strategic line followed in this approach guides us to put high energy into sample evaporation and atomization, so as to break chemical bonds efficiently. Energy input into the excitation process should be limited to the necessary amount to obtain the best signal-to-noise ratio. This strategy is realized in furnace atomic non-thermal excitation spectrometry FANES by glow discharge excitation, in twin furnace techniques in ET-AAS, and in several coupling techniques using laser ablation for direct sampling of solid matter, in combination with atomic absorption, atomic fluorescence, atomic emission and mass spectrometric detection [22,25].

Suspension technique. The "slurry-" or suspension technique is an important approach for direct analysis of solid matter by inductively coupled plasma ICP-optical emission, ICP-mass spectrometry, or flame AAS. Aqueous suspensions of finely grained powders are prepared and nebulized for direct excitation in an ICP [26]. In that way, a technique for trace analysis has been developed with excellent potential. To apply this technique, one must comply with several requirements: (1) grain size must below 10 μm, (2) grain

size distribution must be narrow, (3) a nebulizer of babington cross-flow type must be used with a flow forced by a peristaltic pump, (4) the way of calibration by standard addition based on aqueous solutions must be checked for accuracy [27,28]. The suspension technique is fast and easy to perform, the sources of systematic error are few in number, because sample preparation is very easy and of little extension. However, problems can arise, among others, by incomplete evaporation of particles in the plasma, or by inertial separation of different particles during their transport motion troughout the nebulizing and transfer system [26]. Experiments proved, that the particle size distribution remained unchanged during nebulization and transport, provided that particles, consisting of , e.g. alumina, did not exceed 5 microns [27]. Of course, a few big particles carry a considerable mass fraction. Then, the calibration can be impaired. Verification of this approach by another independent procedure is indispensable.

Nuclear activation analysis. Of the radiochemical methods, activation analysis must be highlighted, providing excellent, but very different power of detection for different elements [29]. Nuclear reactor facilities are required, and total times of analyses can be several weeks, depending on radionuclide half-lives. Even more important, considering the high level of competitive methods, is the outstanding potential, to use radiotracers and nuclear activation in methodological studies for optimization and verification of individual steps of procedures for innovative advancement of trace analysis [8,30].

In total reflection X-ray fluorescence TXRF a specialized geometry of the primary X-ray beam is utilized to apparently eliminate the spectral background originating from scattering of primary radiation at the sample bulk in conventional XRF. A very small angle of incidence below ca. 0.1° guarantees for total reflection of the primary radiation on the plane surface of the sample carrier. Only very thin samples (nm to several μm, depending on the atomic number of the matrix) on top of this target can be irradiated. Owing to the decreased background, the power of detection is improved by 3 orders of magnitude, as compared to conventional excitation. Thus, TXRF is qualified to reach the picogram-range, in the direct micro-trace analysis mode of thin sections (e.g. freeze dried tissue), as well as in extreme trace analysis involving preconcentration steps, from dry residue of minute amounts of solutions (see Fig.5). Since this is a microanalytical technique, bulk analysis of solids meets severe limitations. What can be easily obtained, is a fast first overview for a semiquantitative information [12,31].

Proton induced X-ray emission PIXE is another technique offering a signal-to-background ratio superior to that of conventional X-ray emission spectroscopy, generally excited by primary electrons in the electron microprobe EMP. Both methods are used with focussed particle beams for X-ray excitation as probe methods [32,33]. The same applies to synchroton radiation-induced X-ray microanalysis SRXRF[34].

Mass spectrometry. Inorganic mass spectrometry MS involves ion sources of very different types, like ICP-MS, glow-discharge-MS, secondary ions SIMS, and others. It represents the most universal determination principle. It offers detection powers in the picogram- and even femtogram-range, in selected cases. It can beneficially apply the isotope dilution analysis principle, so that very good accuracy can be obtained. ICP-MS allows for a powerful multielement determination from dilute solution volumes above 0.1 mL. The detection power is superior to that of ICP-OES by 2 to 3 orders of magnitude, thus reaching the µg/L- to ng/L-range. In ICP-MS, restrictions appear where ion-clustering interferes with analytical lines. Further problems may result from memory effects and matrix effects. This presents a challenging task for future improvements [26]. Combination with separation procedures is possible for element speciation analysis procedures.

Probe methods. Even higher is the absolute power of detection of the extreme microbeam methods for thin film analysis on top of solid matter. This region of absolute power of detection at the picogramme- and attogramme-level is reached by bulk analysis only quite exceptionally, even by neutron activation analysis. One of the most important characteristic features of those techniques is the local resolution. For a more detailed discussion of the characteristics of probe methods for thin film analysis, see [3,35].

For the future, one can predict that particularly laser evaporation of solid matter of environmental origin will take an important significance, when the time will bring up cheap semiconductor diode lasers to combine with atomic absorption, atomic fluorescence, atomic emission and mass spectrometric detection [36]. The possibility to evaporate small domains from a bulky solid sample opens new ways for local microanalysis in the 5-micrometer range [25], since it also applies to non-conductive matter [37], such as soils, dust, and organic matter. Additional secondary excitation by a sparc, an ICP, or a microwave field yields detection limits in the µg per g range [17,22,25,36]. These are

microanalytical techniques, consequently the problem of calibration will be a very significant one, again. The formerly serious problem of insufficient reproducibility of laser-ablation has been successfully solved by adjusting the conditions for formation of the laser plume to about 100 mbar of inert gas, by laser pulses of low energy [25,36]. Benefit from time-resolved detection of spectra is based on exclusion of the initial formation of the plasma plume, which corresponds to the phase of a high background level. The excellent absolute power of detection is estimated to $5x\ 10^{-15}$ g [38].

Another very important innovation is the application of laser-spectroscopy including laser atomic absorption spectrometry LAAS [22,23], laser induced fluorescence LIF, laser enhanced ionization LEI, field ionization laser spectrometry FILS, resonance ionization spectrometry RIS and resonance ionization mass spectrometry RIMS [22]. Recently, resonant and non-resonant multi-photon-ionization of sputtered neutral atoms were made the base of one of the most sensitive surface-analytical techniques, viz. sputtered neutrals time-of-flight mass spectrometry TOF-SNMS in the imaging version. It offers a local lateral resolution of about 1 μm in the static SIMS-mode, which means at a negligible rate of surface damage. The sample amount consumed is only about 1 % of an atomic monolayer. This is feasible by means of the tremendously efficient exploitation of the ablated particles, firstly by saturation applying two lasers, secondly by the high yield of ion-detection in a TOF-MS instrument [39,40].

Immunoassay. Another field of growing importance is the application of immunoassays for determination of both organic and inorganic pollutants, particularly for the purpose of fast screening of a multitude of environmental samples. The reader is referred to excellent comprehensive reviews [41,55].

5. Anthropogenically mobilized element traces; example Hg

As an example let us consider one problem, which is caused by the omnipresence of the elements in all matrices in connection with the anthropogenic enrichment of elements in our environment, worldwide [4]. Along with Cd, Pb, Tl, and As, **mercury** is one of the most important problem elements which pollutes the environment (see Fig.6). Due to its high volatility and toxicity, it endangers the conditions of life. It is released by

anthropogenic activities, in addition to considerable basic emissions from natural sources, namely by volcanic activities and weathering of rocks.

In industrial areas worldwide, large amounts of mercury are being emitted into the atmosphere, in the stages of production and applications of mercury and its compounds. These amounts, however, can be well controlled today. The main problem, which mostly will be overseen is, that even much more mercury is emitted by its release during all combustion or heating processes of all raw materials removed by mankind from the earth crust (e.g. coal, fuel, ores) or of organisms (e.g.plants, animals). Its ubiquitous concentration in these materials is in the middle ng/g-range. Growing industrialization has led to an increase in these emissions that are unavoidable in our industrialized society. The amount of mercury emitted into the biosphere amounts globally to approx. 10.000 tons per year at present (Table 2).

With an increase of the world population, up to now, this uncontrollable amount of mercury released in this way undoubtedly accumulates. Therefore, nobody can predict today how this increasing Hg-emission will affect the health of living individuals of future generations. To a less serious degree, this also applies for all other easily volatilized elements. The main reason for this fact is that the ecological cycle of mercury is very complicated (Fig. 6) and that its physiological impact differs with the various chemical compounds in which it appears. As we know today, mainly the organo-mercury compounds which enter the human nutrition chain via water are physiologically relevant. There is for example, a strong enrichment of methyl-Hg-compounds in fish. On the other hand, little is known about the mobility of Hg and its compounds in soils, which take up again the mercury from the atmosphere. In order to distinguish natural concentrations from elevated concentrations of anthropogenic origin, we must be able to reliably determine mercury-contents of all environmentally relevant matrices. A detection power down to the lower pg/g range is needed, at least for organic matrices. The problems of systematic errors due to contamination, adsorption and evaporation were encountered during the solution of this supposedly simple task.

Massive analytical problems here already start at the apparently simple steps, as during storage of liquid samples. For studies in adsorption at the walls of the sample containers, radiotracer technique offers a unique potential. Using mercury-203, we can not only determine the loss from the solution (see Fig.7), but also the adsorbed amount from the

emptied container (see Fig. 7B), and this is done even in the nanogramme regime [43, cf.42] ! Drastic Hg-losses appear from water, but also from diluted acids (Fig. 7). Hydrochlorid acid is already useful to stabilize the contents, but only HCl/ hydrogen-peroxide yields constant mercury-concentrations during ten weeks. A possible explanation is the formation of stable Chloro-peroxo-mercury-complexes. Further investigations demonstrated that not only adsorption, but also volatilization was responsible, penetrating first of all polyethylene, but also polypropylene. Reduction to the mercury(I)-state, followed by a disproportion into volatile mercury(0) or organo-mercury, obviously represent important steps in this penetration process [43]. Sources of error from all other stages of the analysis are also effectively checked using radiotracers, from the decomposition to the final measurement [7,22,30].

In Fig. 8), typical vertical profiles of mercury concentrations in various soils show that there is a strong enrichment of mercury in the upper layers of all soils. This enrichment originates from anthropogenic mobilization. It can be clearly distinguished from the naturally formed Hg-deposits in the underlying layers. Soil from high bog is considered as a relatively simple model system. Mercury can arrive at the bog soil only via the atmosphere. Profiles show a natural background of ca. 20 ng/g in greater depth, below about 0.7 meters. In the upper horizons, the anthropogenic portion is added. In the near surface levels, an equilibrium is recognized between input from the atmosphere and return of mercury from the soil into the atmosphere. Using radioactivily labeled mercury it was demonstrated that about 15 % of the mercury taken up by the high bog was released again in the form of metal vapor or methylmercury.

It was more difficult to answer the question as to the properties of the mercury that was retained by the peat bog soil. The isolation of the mercury compounds formed in the peat bog soil was achieved by employing a separation system using high-pressure liquid chromatography coupled to a microwave-induced plasma optical emission detector. Thus, it was possible to identify the most common mobile mercury-compound occuring in the peat bog soil. By using UV-, IR- and NMR- spectroscopy, it was found to be mercury humate.

A general extrapolation of enrichment of mercury would indicate the danger of man-made Hg-intoxication. In addition to the greenhouse effect, this risk presents another strong argument to minimize the use of fossil fuels [4]. In conclusion, the problem of Hg-

enrichment is probably less severe than assumed by the estimations given before, since Hg is strongly bound by compounds in the soil and even is partly remineralized. During these processes, one also has to consider the presence of concomitant elements such as sulphur and, first of all, selenium, which possess strong binding capacities for Hg forming highly insoluble compounds such as sulfides and selenides. Therefore, also the trace analysis of Se must be studied in detail [4,6].

Another example illustrates a close relationship between environmental, medical and analytical problems. To minimize environmental risks, platinum catalysts were introduced into automobile engines. These catalyzers greatly contribute to a decrease in the emission of NO_x, PAHs, etc. However, by this reduction of emission, another type of emission will appear: small amounts of platinum are released and accumulated in the environment. The three-way catalyzer-systems used in Germany, Europe and elsewhere release concentrations at the mean to upper ng/g level per kilometer [2].

The environmental impact of the newly introduced possible risk caused by wide-scale mobilization of this basically rare element is not predictable today. With the present knowledge, general conclusions concerning its physiological effects, including possible detrimental effects and health risks (cancer, platinum asthma, platinosis) cannot be drawn. Lack of information about distribution and Pt-speciation in the environment causes analytical studies to be performed as a base for the estimation of any of those risks. Since natural omnipresent concentrations of platinum are of the order of 10^{-8} to 10^{-9}%, such studies are just in their initial phase, and they have turned out to be extremely difficult [2,45].

6. Element trace determination

6.1 General strategy

In the bulk-analysis at trace levels in environmental matter, the aim is to develop direct instrumental determination procedures, that are economically favourable and beneficial, i.e. simple, quick and inexpensive (as indicated in Fig. 9, left hand side). In the long term run, results are obtained truly beneficially only, if they are accurate and of guaranteed reliability [4,10,11,42,44]. Several detrimental effects have to be avoided that are primarily caused by blanks and by non-linear calibration functions. To achieve this, standard reference materials SRM are strictly required for correction of matrix effects, and for accuracy control of the instrumental procedures, in most cases. Today, such reference

materials are not always certified for its elemental contents on the extreme trace levels, or even not yet attainable in sufficient variety [45]. In solid matter, reliable determinations are often restricted to the µg per g-level. To cope with this situation requires the expenses of wet-chemical combined procedures (see Fig. 9, right hand side). The procedure is split up into single steps. Every step is small enough to study its individual yields and error sources, and to eliminate all systematic errors, in a troublesome process. To achieve the optimum of reliability and of power of detection, the trace element to be determined must be prepared for analysis, in an isolated form in an excitation volume as small as possible [42,44]. Multi-stage procedures via solutions or gas phase may overcome problems due to sample inhomogeneity in bulk analysis. Further, they are easy to calibrate by means of standard solutions. Such reliable procedures can be utilized in a certification campaign [46] for reference materials, provided that agreement is obtained with the results of several independent combined procedures, that are individually designed to depend on completely different sources of possible errors [1,42,46,47]. Traceability aims, in some way, to the recursion of the analytical calibration problem back to a simple system that can be calibrated by means of aqueous standard solutions, or carefully weighed high purity materials, and clean solvents.

The systematic study of sources of different systematic errors (see Fig. 9) takes an important position here. It requires not only a high work-load, but also the proper ideas, because there is no means to guarantee, that all systematic errors have been avoided completely. There is, however, means to enhance the degree of certainty. First, one has to discern and investigate the systematic errors of each and every single step. Results of interlaboratory comparisons demonstrate, that the relative systematic error increases with decreasing levels of concentrations [4,44,46,47]. Systematic deviations of one order of magnitude from the true concentration values are no exception.

The causes of systematic errors are very difficult to trace and to avoid. This task requires a lot of expertness, so there is a need for more intensive training. Certainly, also combined procedures include systematic errors, but those are easier to discover, due to their different causes, see Fig. 9 and Fig. 10. The main problem here is contamination due to the omnipresence of the elements. Therefore, a lot of effort has to be invested into minimizing blank values from equipment, reagents and laboratory air, in all steps of a procedure. Realistic detection power of analytical procedures is often limited by blank values and their fluctuations which may surmount multiply the extrapolated theoretical

detection limits of the determination method, under idealized conditions, particularly in the case of more abundent elements, cf. Fig. 10.

Measures to limit blank values introduced from the most important sources of systematic error focus onto cleaning procedures for (a) the analytical reagents, (b) the analytical vessels and instruments, and (c) the laboratory air and environs [42,44]. The choice of the analytical procedure should consider that only such solvents and reagents are involved that are easy to purify, preferably by distillation or sublimation. Particularly solvents are often used in considerable excess, so highest purity is essential here. Best results are obtained, when the process of distillation is optimized so that formation of any aerosols is completely avoided that carry the initial composition of the educt. Since this aerosols generally form during the boiling process, the preferred preparation procedure uses mild heating to temperatures well below the boiling point to volatilize the solvent from the surface without the boiling process or any violent agitation, by subboiling distillation, as shown in Fig. 11. The efficiency of this procedure was checked by TXRF and radiotracers in our laboratory.

The number of vessels and tools in contact to the sample must be restricted to a minimum. Also the choice of the vessel materials should consider that they must be easy to purify, which requires high purity materials with very smooth surfaces and of the smallest suitable size to minimize its surface area. Suitable materials are fluorinated polymers (PFA, PTFE) and preferably fused silica, as applicable. Extensive experiments have proven that these materials are best purified in view of metal trace contamination. The optimum procedure for general cleaning is based on subjecting the vessel for some time, at the highest possible temperature, to the cleaning acid or water of the highest available purity. This is achieved in a steaming apparatus (shown in Fig. 12), where the vessel is rinsed for several hours with the freshly distilled vapor from a pure acid. Afterwards, the surface of the material is equilibrated for two hours in water vapor in a similar apparatus to reduce the surface activity and adsorption. The vapor tubes contacting the vessel are also made of fused silica.

To reduce contamination from the laboratory air to a minimum, cleanroom laboratories are the optimum choice [42,44]. However, these are very expensive, and similar effects can often be achieved by a very careful combination of other measures, combined of tightly closed systems (see Fig. 13 for an example), clean air hood working benches,

double containers, care for cleanliness in an ordinary laboratory, and, last but not least, thorough planning of the execution of any analytical procedures to avoid any import of contamination. Even a cleanroom laboratory is of benefit only, if stringent working rules are obeyed considering such additional measures. Certainly, the effort necessary in this direction is completely dependent on the particular element and on the concentrations to be determined in relation to its level of omnipresent concentration. The most important remark in that respect is: It will be definitely useless to install an expensive instrument for elemental trace analysis, as for example an ICP-mass spectrometer, in a place close to the air outlet of the air conditioning or a refrigerator, as I have observed recently in a laboratory in Germany. It is an important duty of the analyst to design carefully the compartment for the sample supply to instrumentation for trace determinations.

This part is concluded by recapitulating [4] the most important rules which help us to overcome such problems in extreme trace analysis mainly caused by systematic errors:

- It is not allowed to generalize or to extrapolate into the extreme trace levels in any way. Each solution of an analytical problem needs its individual strategy.

- In extreme trace analysis, the uncritical use of direct instrumental methods may not always yield better results, but its opposite, if systematic errors are not perceived.

- Optimal power of detection and optimal reliability are only achievable if the trace element to be determined is prepared in isolated form on the smallest possible target area or in the smallest possible excitation volume, for excitation of the analytical signal.

- Most carefulness must be spent to the problems (a) of contamination and adsorption causing positive systematic errors and (b) to desorption effects and volatilization of the elements causing negative errors.

- All results obtained from a single method must be confirmed by those of an independant second or third method before we can rely upon them.

6.2. Nuclear Methods

The main fields of application of powerful nuclear methods of analysis result from consideration of economy, on the one hand, for big series of samples. On the other hand, nuclear methods are useful in establishing and controlling accuracy and reliability. They are particularly useful, where other methods are hampered by matrix effects, insufficient selectivity, or are limited by blank values [7,8,29,30,50]. It is especially the problem of blanks and unknown yields at trace levels that can be checked excellently by radiochemical techniques [4,42,44,47].

In Fig. 14, an example is presented from the biggest field, i.e. from activation analysis. In all techniques of activation analysis (cf. [29]), the analytical sample of 10 mg to 1 g, after drying, is subjected to an irradiation. Mostly used are reactor neutrons, but also fast neutrons, charged particles from an ion accelerator, or gamma-radiation. These induce nuclear reactions which produce indicator nuclides of numerous elements in the sample. These can be measured directly from outside, so that the risk of blank values is minimized in this analysis. Reactions are chiefly of (n, γ)-type, producing β-emitting isotopes of the irradiated element nucleus. As an example, the analytical scheme for instrumental activation analysis of airborne particulate matter collected on filter material allows for determination of 30 to 40 elements from two irradiations of 5 min and 5 h, resp. (Fig. 14). In general, problems due to matrix effects do not appear. Filter material must be carefully selected according to their blank levels, and frequently checked. In biological tissue, high Na-contents produce high levels of background radiation originating from Na-24 that often represents 99% of the total activity. This requires its chemical separation, after decomposition of the activated sample [29].

Another important task is the determination of element traces in rain water, river water, sea water and ice drilling cores. In this field, nuclear methods are of no particular benefit, because the advantage of direct irradiation do not apply to water samples. Today, the broad variety of all wet-chemical determination methods can be applied alternatively. Here is no advantage of nuclear methods by avoiding any sources of systematic error, and blank levels are as low as with other methods applied [8,29,30]. Often, high activities of Na, Cl and Br interfere. Elemental distribution in the sub-millimeter range can be efficiently determined by autoradiography of activated samples. E.g., the distribution images (see Fig. 15, from [50]) of manganese in leaves of cotton show significant differences between a healthy plant and an injured plant from an unfavourable soil.

6.3. PIXE

Also ion beam analysis can be helpful in identifying systematic errors - already at the stage of sample preparation. This is exemplified in the case of microanalysis using proton induced X-ray emission PIXE, at a lateral resolution of ca. 1 μm. Numerous efforts have been undertaken to record the elemental status of animals sampled from an ecosystem [51, see reports on specimen banking in this volume], but also of human individuals and patients, by means of simple monitors. The analysis of hair strands, as well as feathers and finger nails has been proven useful for the determination of poisoning by heavy metals. Essential elements are enriched in samples of blood and tissue. However, elevated contents are present in hair and nails, of those elements that are drained off from the organism. Environmental loads by Hg, Cd, Pb, Se, Sb, As can be detected simply, painless, non-invasive and without any administrative licence. Additional benefit results from the fact that hair, growing for some period, accumulates element traces and displays a deposit for a retrospective analysis.

An important objection against any uncritical utilization of those monitors is raised due to their high risk of contamination. It is well known that workers occupied with handling of gold-pieces exhibit high levels of gold on their hair strands caused by external contamination. However, precisely the trial for careful cleaning hair strands before the analysis, may falsify the analytical result.

On the example of the essential trace element Se, enormous scatter of data from different persons had been detectet, whereas reproducibility was good for individuals [52]. The effect of shampooning was studied. The Se-distribution across a single hair strand was monitored applying PIXE microanalysis on the μm-level, see Fig. 16 [52]. The result was that Se had been diffused, from the Shampoo (containing S to help against skurf, and Se was accompanying sulfur). The outer 5 to 10 μm layer of the hair strand contained 10 to 20 μg/g Se, whereas in the center the concentration was about 3 μg/g. The thickness of the contamination layer indicated that Se had been diffused. For the determination of the low levels of Se of the non-treated center of the hair strand, the detection power of micro-PIXE was found insufficient [52]. With such high levels of Se in the outer region, also interferences must be considered in the determination of elements that are strongly bound to Se. From the distribution of trace elements in a cell, information should be derived about the physiological dynamics inside, about accumulation and draining off of harmful substances and metabolites. Micro-PIXE is

qualified to analyze and to correlate the distributions of several elements in thin sections from tissue, e.g. from rats liver.

PIXE has been and still is employed to analyze airborne aerosols, in several routine network measurement programmes [32,33,53]. Conditions are best analyzing thin layer samples of less than about 10 μm. We have carried out such analyses in the frame of meterological programmes in Frankfurt. Aerosols are best sampled on membrane filters or size-fractionated, using small impactors. Predicatory results were obtained concerning aerosol transport on the short-range as well as the long-range scale, see Fig. 17, from [53].

7. Conclusion

In this survey of analytical developments important for application in ecological research, I have only touched the field of established routine analysis, although it deserves due regard. For future advancement (see Table 3), the enhancement of the power of detection, in absolute terms, takes a very important position, particularly in view of the examination of species-fractions as well as of microdomains. The basic reason for that is not at all to induce lower and lower threshold values in legislation, as is sometimes stated as an opinion. The reason is to contribute to the best of reckoning environmental risks. Analytical chemistry has to contribute to the protection of the quality of life (see Fig.18). For this aim, there is a stringent requirement to learn the right balance with the technological progress. Technological progress is inevitably connected to risks and consequences on man and environment. Such risks must be recognized in due time, estimated, and minimized. Analytical chemistry takes a very important position in both fields, namely technological progress and estimation of risks. In both fields, complex systems of substances must be regarded. Informations concerning these systems of substances form the base of decisions. Therefore these data have to be reliable data. It is very important that these data are transferred objectively, and interpreted objectively in collaboration with other disciplines. If objective competence is missing, giving publicity to just data without interpretation may induce reservations and fears in public. Thus, elucidation is another important duty of environmental analysis.

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Figure captions

Fig.1 Ambivalent physiological dose-effect relationship of an essential trace element (according to [4]).

Fig.2 Comparison of the means of some concentrations in serum, determined in the period before 1976 and after 1976 (from [4] according to data assembled by *Versieck* et al.[54])

Fig.3 Criteria of improvements in micro and trace analysis. All these characteristics are closely interconnected with each other [3].

Fig.4 Typical figures for the power of detection in absolute terms (top) and for the working range on a relative concentration scale (bottom) of different methods used for trace analysis of ceramic materials (modified from [12]):

X-ray fluorescence analysis XRFA
titrimetry TITR,
voltammetry VOLT,
optical emmission spectrometry by sparc or arc OES-SP/A,
inductively coupled plasma-optical emission spectrometry ICP-OES,
flame atomic absorption spectrometry FAAS,
neutron activation analysis NAA,
total reflection X-ray fluorescence analysis TXRF,
glow discharge mass spectrometry GDMS,
electrothermal atomic absorption spectrometry ET-AAS,
inductively coupled plasma mass spectrometry ICP-MS,
electron microprobe EMP,
Auger electron spectrometry AES,
secondary ion mass spectrometry SIMS.

Fig.5 TXRF spectra of NBS 1577 bovine liver and 1573 tomato leaves. (from [31])

Fig.6 The circulation of mercury in the enviroment (according to [4]); u.a. = and other gases

Fig.7A Volatilization of Hg from aqueos solutions (0.5M HNO_3, 2 ng/ml ^{203}Hg, PTFE

shampoo. X-ray emission analysis with a proton microprobe PIXE (from [52]).

Fig.17 Long-range transport of particulate aerosol matter across Europe (from [53]).

Fig.18 Balance of technological progress and risks associated with this progress. Principal tasks of analytical chemistry comprehend generation of reliable data from both fields, but also objective interpretation of these data in an interdisciplinary team-work, as well elucidation to the public.

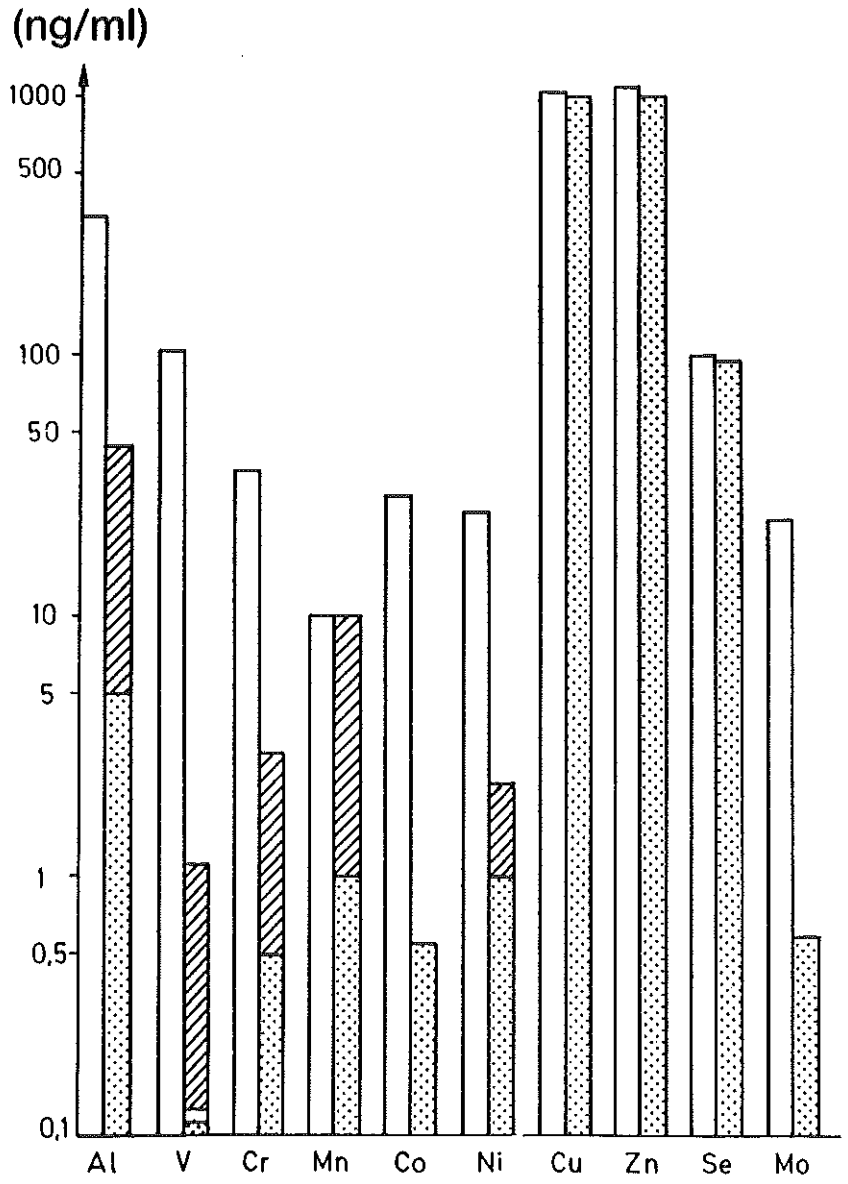
Table captions

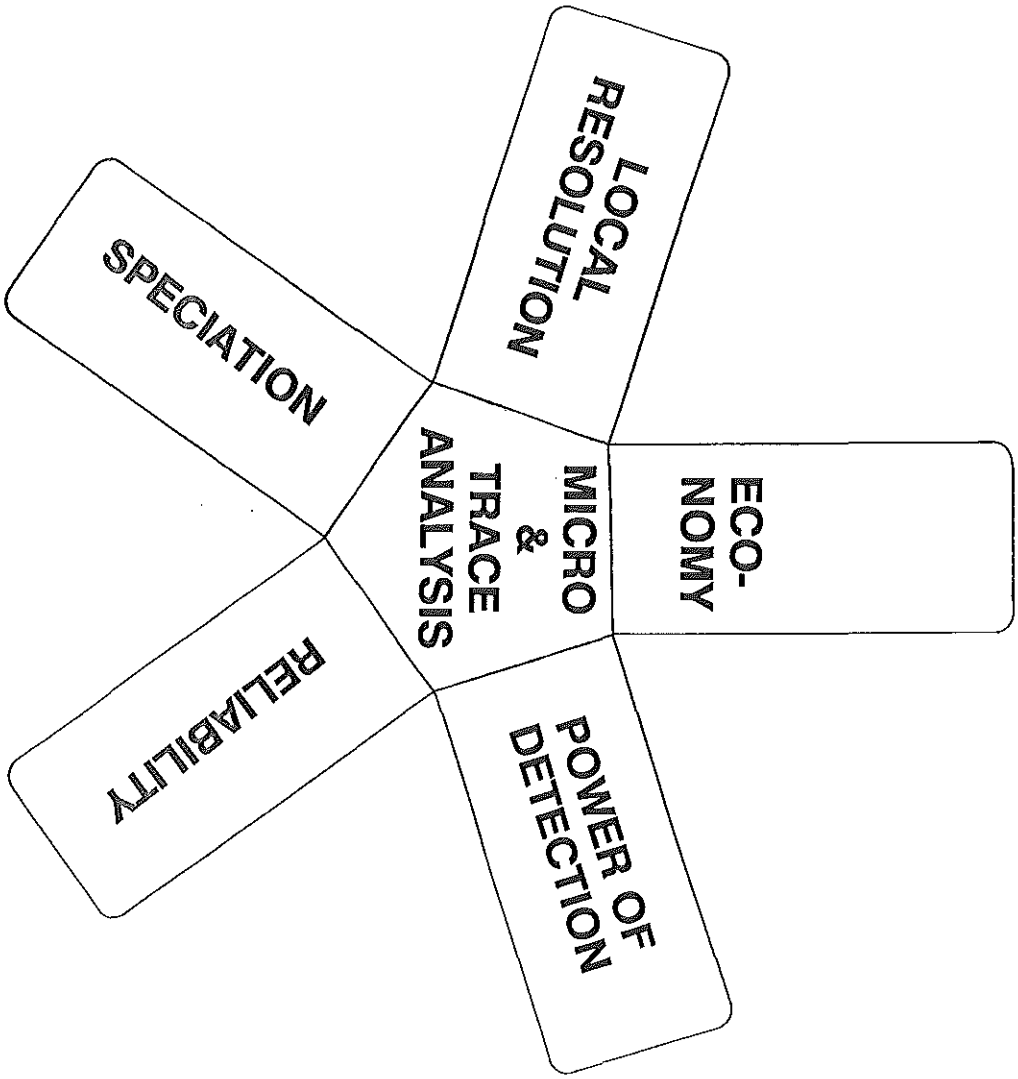
Table 1: relative elemental abundances in magnetic rocks (according to Taylor, 1964)

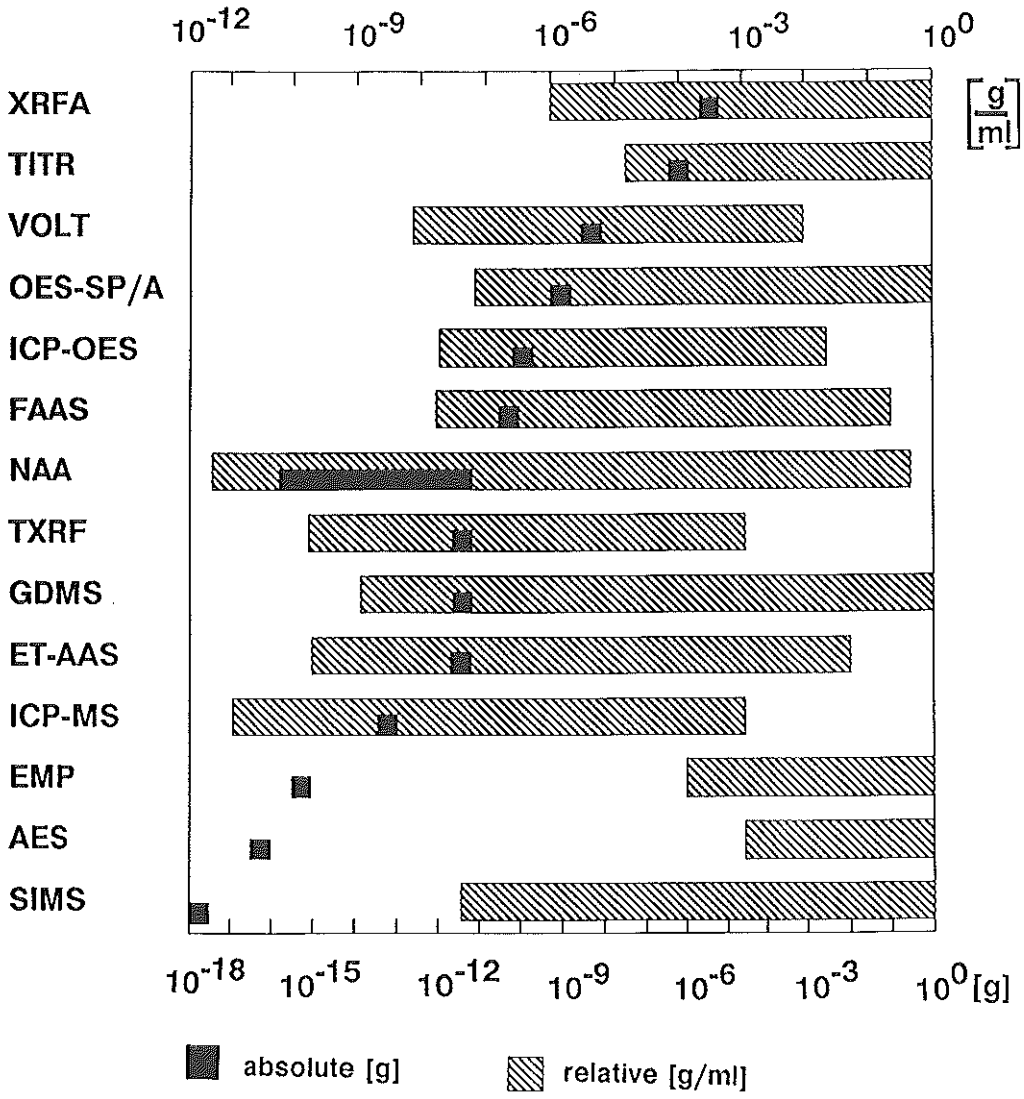
Table 2: Comparison of global mercury emissions of natural and anthropogenic origin (modified from [4], based on data from 1970 and 1974).

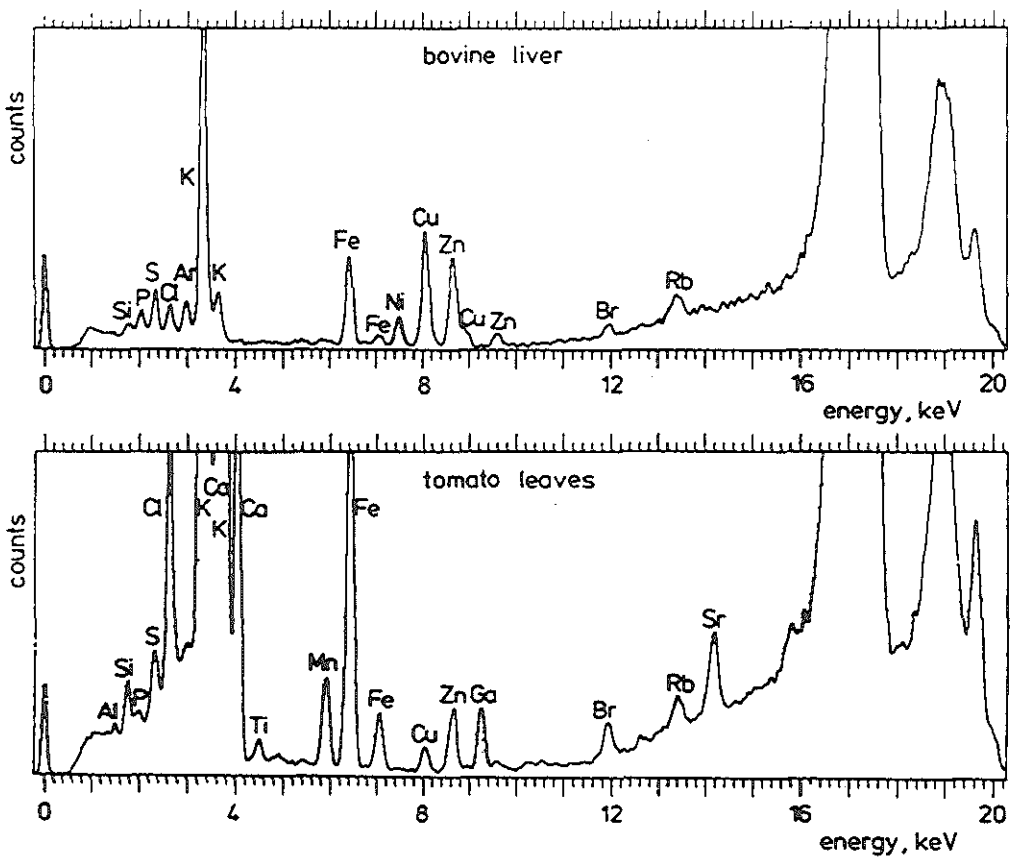
Table 3: Future tasks on advancement of micro- and trace analysis of enviromental matter.

disease
- death
deficiency
symptoma
HEALTH
toxic
effects
disease
- death
physiological effect
concentration of trace element

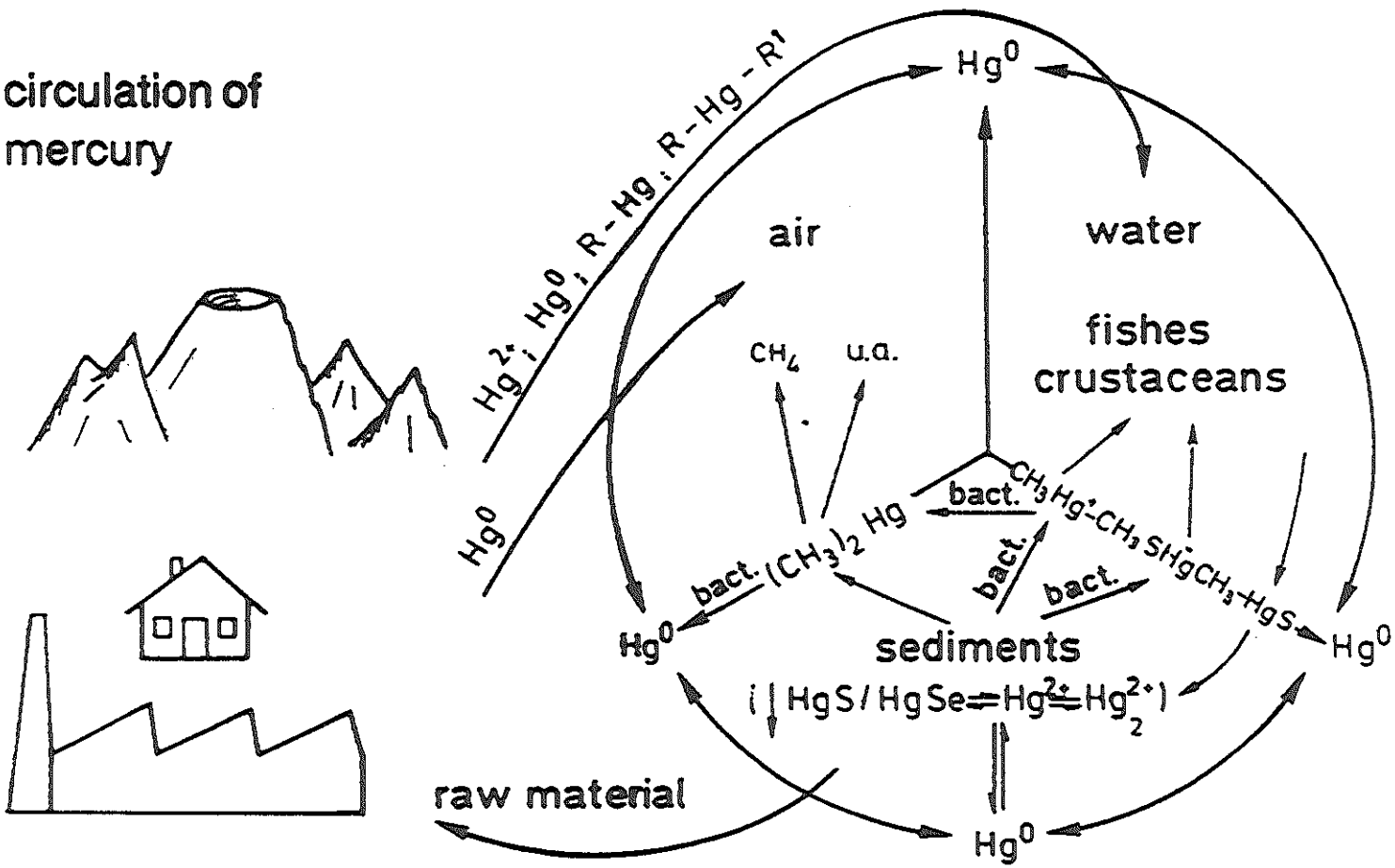

(ng/ml)
1000
500
100
50
10
5
1
0,5
0,1
Al
V
Cr
Mn
Co
Ni
Cu
Zn
Se
Mo

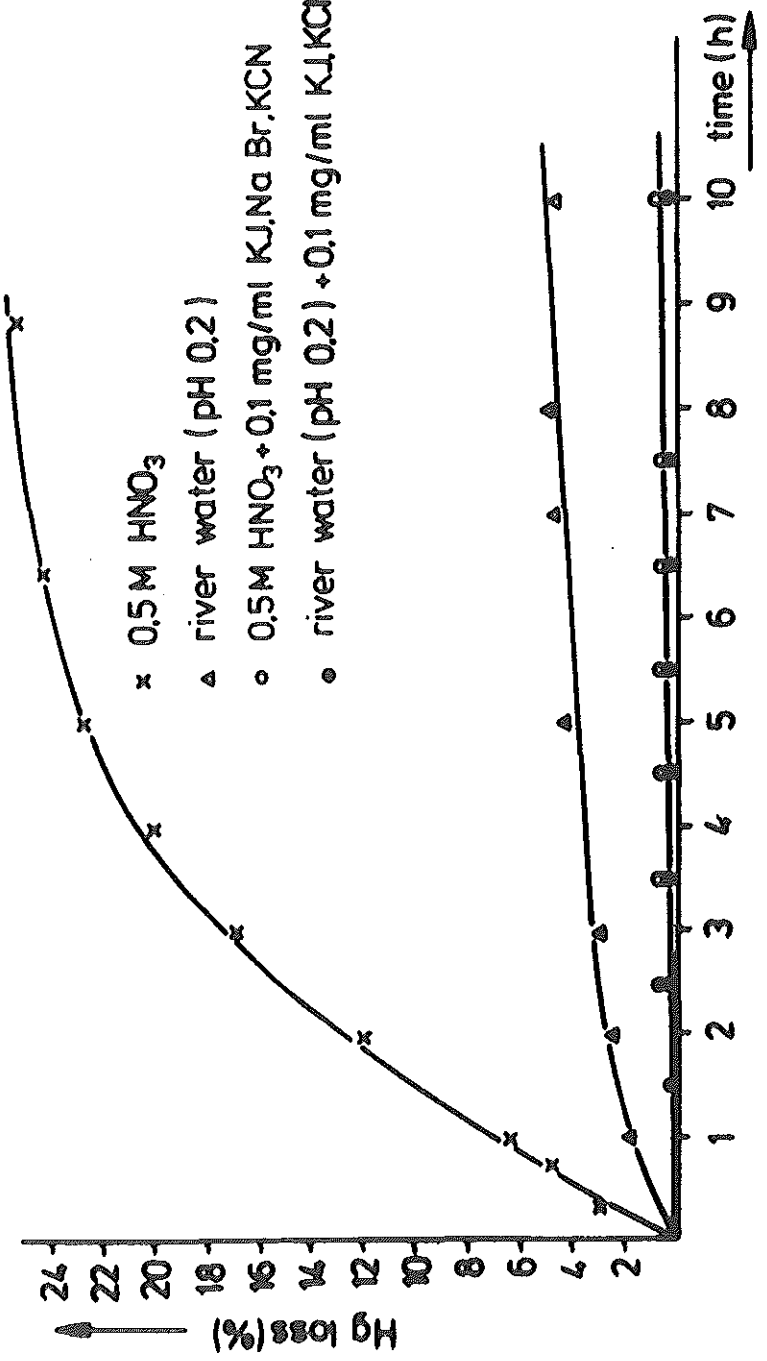

LOCAL RESOLUTION
SPECIATION
MICRO & TRACE ANALYSIS
ECO-NOMY
RELIABILITY
POWER OF DETECTION

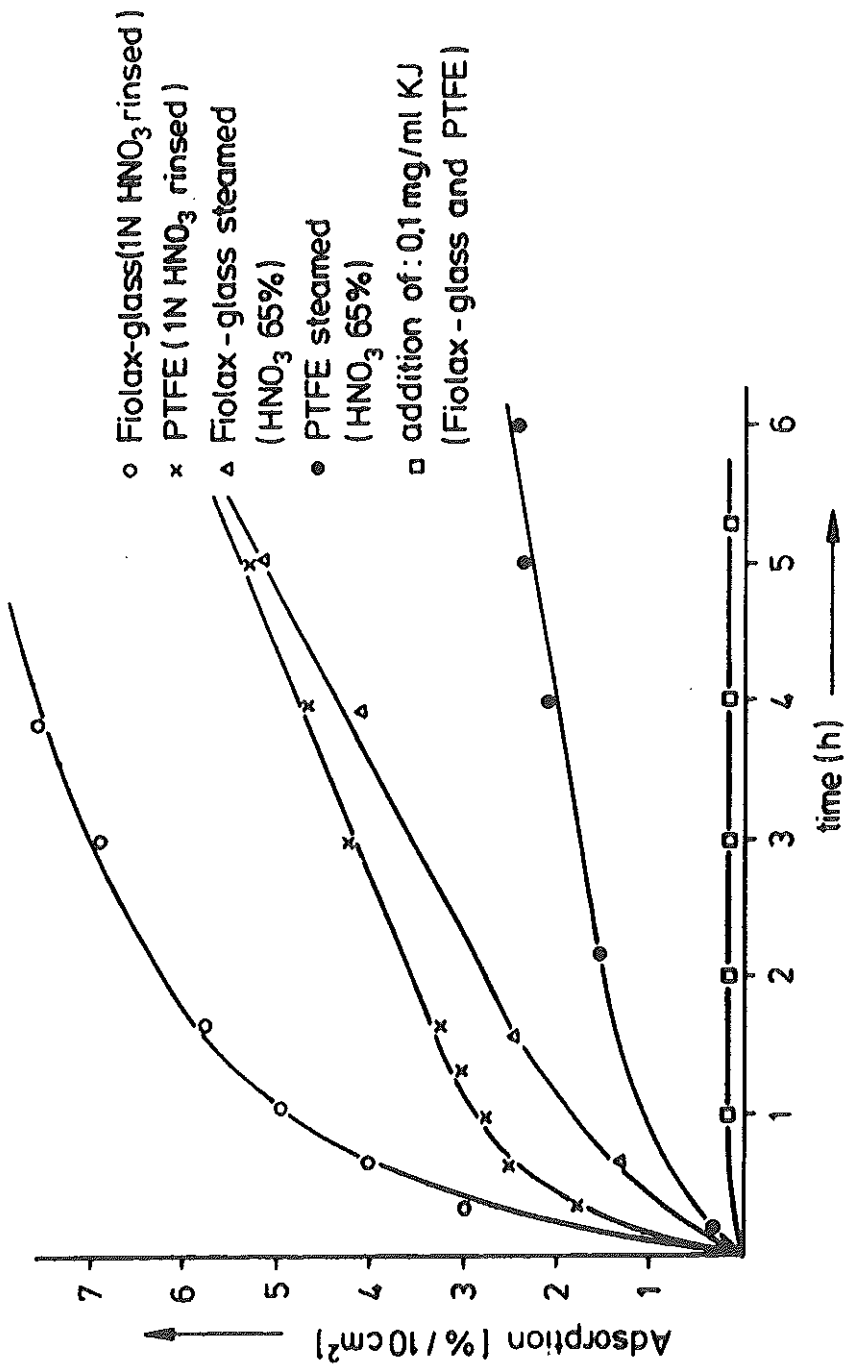

10-12
10-9
10-6
10-3
100
XRFA
TITR
VOLT
OES-SP/A
ICP-OES
FAAS
NAA
TXRF
GDMS
ET-AAS
ICP-MS
EMP
AES
SIMS
[g/ml]
10-18
10-15
10-12
10-9
10-6
10-3
100 [g]
absolute [g]
relative [g/ml]

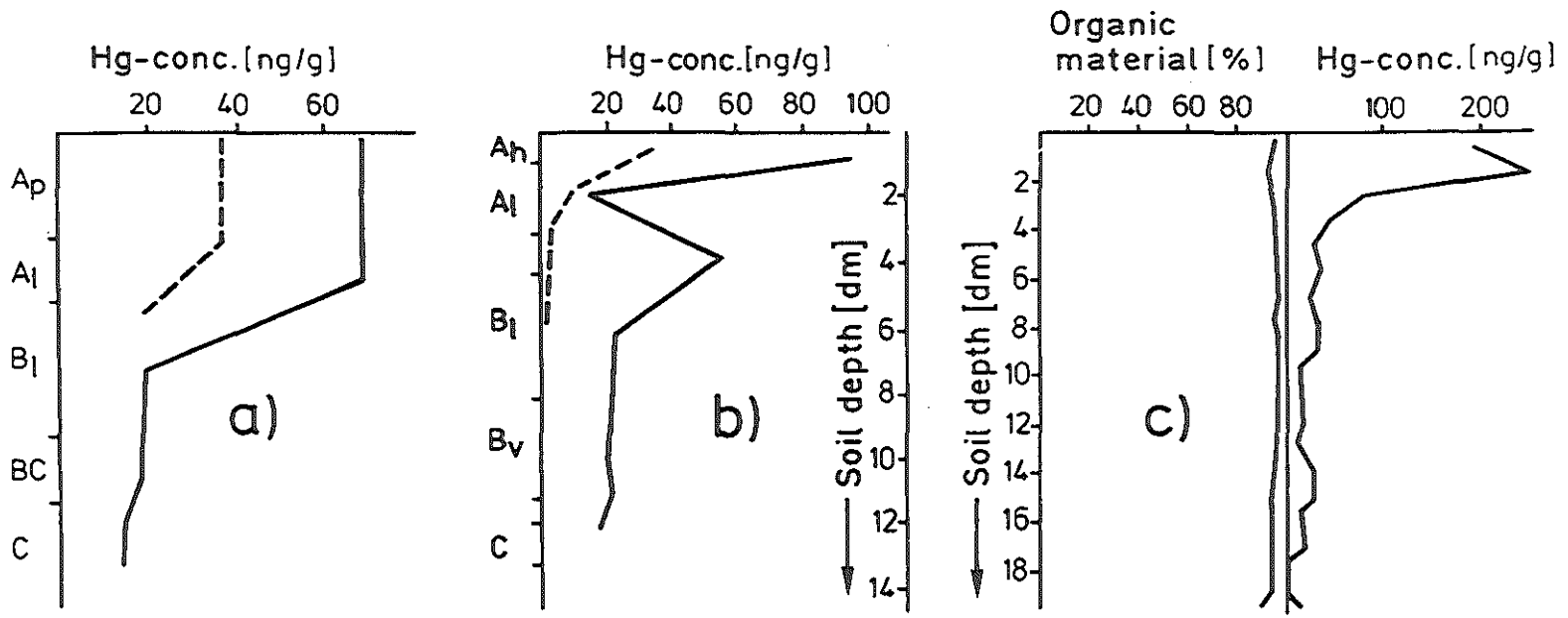

bovine liver
counts
K
Fe
Cu
Zn
S
Ar
K
Si
P
Cl
Ni
Fe
Cu
Zn
Br
Rb
0
4
8
12
16
20
energy, keV
tomato leaves
counts
Cl
Ca
K
K
Ca
Fe
S
Si
Mn
Sr
Al
P
Ti
Fe
Cu
Zn
Ga
Br
Rb
0
4
8
12
16
20
energy, keV

circulation of mercury

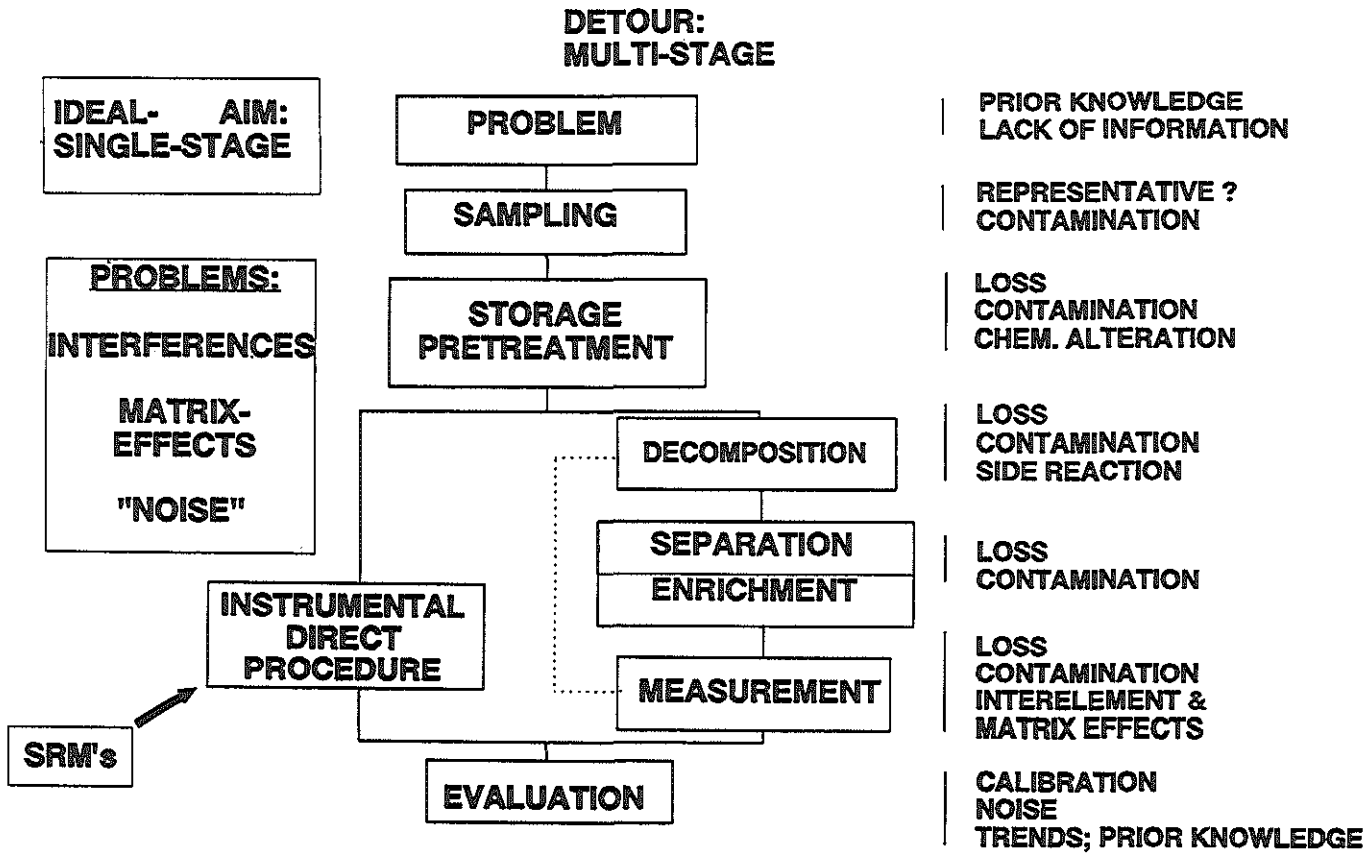



Hg loss (%)
24
22
20
18
16
14
12
10
8
6
4
2
1
2
3
4
5
6
7
8
9
10
time (h)
× 0,5 M HNO3
▲ river water (pH 0,2)
○ 0,5 M HNO3 + 0,1 mg/ml KJ, Na Br, KCN
● river water (pH 0,2) + 0,1 mg/ml KJ, KCN

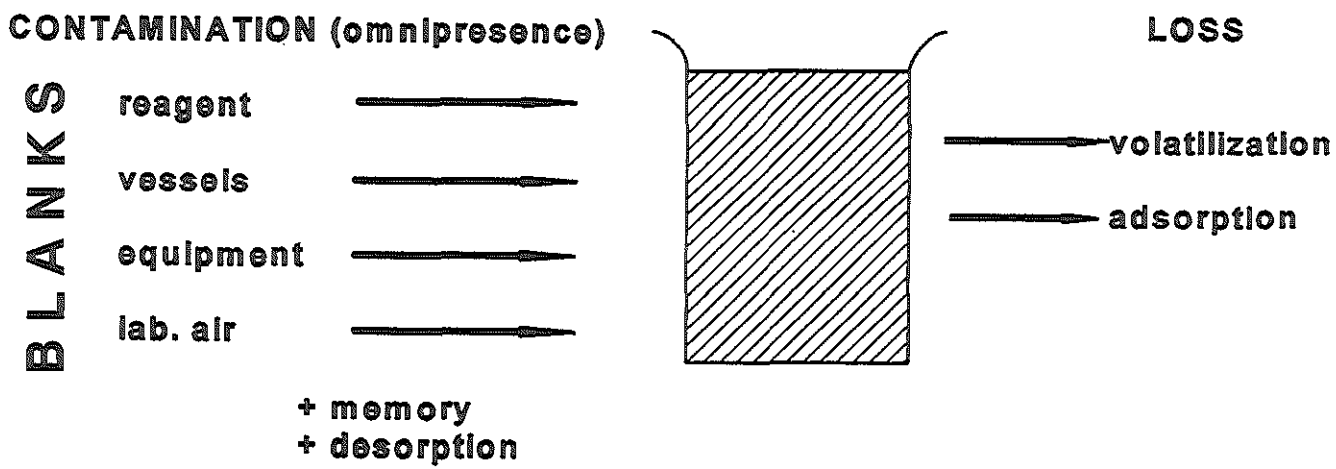

o Fiolax-glass(1N HNO_3 rinsed)
x PTFE (1N HNO_3 rinsed)
Δ Fiolax-glass steamed (HNO_3 65%)
• PTFE steamed (HNO_3 65%)
□ addition of: 0,1 mg/ml KJ (Fiolax-glass and PTFE)
Adsorption [% / 10 cm²]
time (h)
1
2
3
4
5
6
7

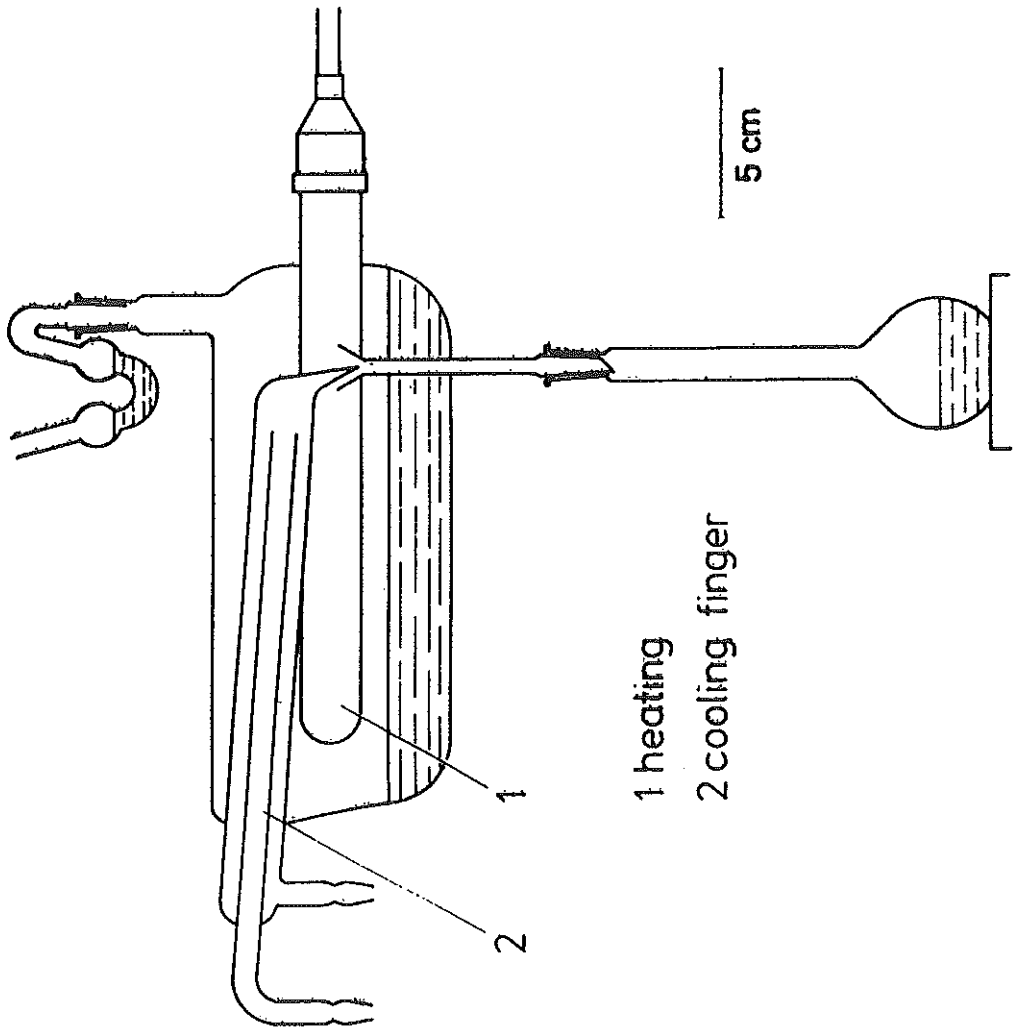

Hg-conc. [ng/g]
20 40 60
Ap
Al
Bl
BC
C
a)
Hg-conc.[ng/g]
20 40 60 80 100
Ah
Al
Bl
Bv
C
b)
Soil depth [dm]
2 4 6 8 10 12 14
Organic material [%]
20 40 60 80
Hg-conc. [ng/g]
100 200
Soil depth [dm]
2 4 6 8 10 12 14 16 18
c)

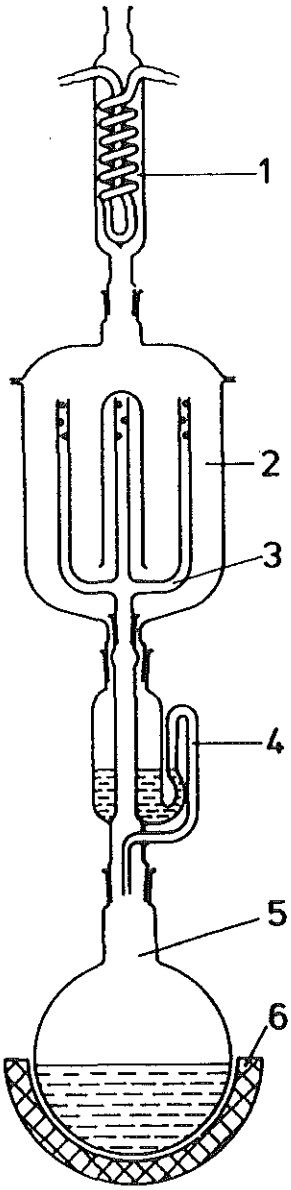
ANALYTICAL PROCEDURES & SOURCES of ERROR



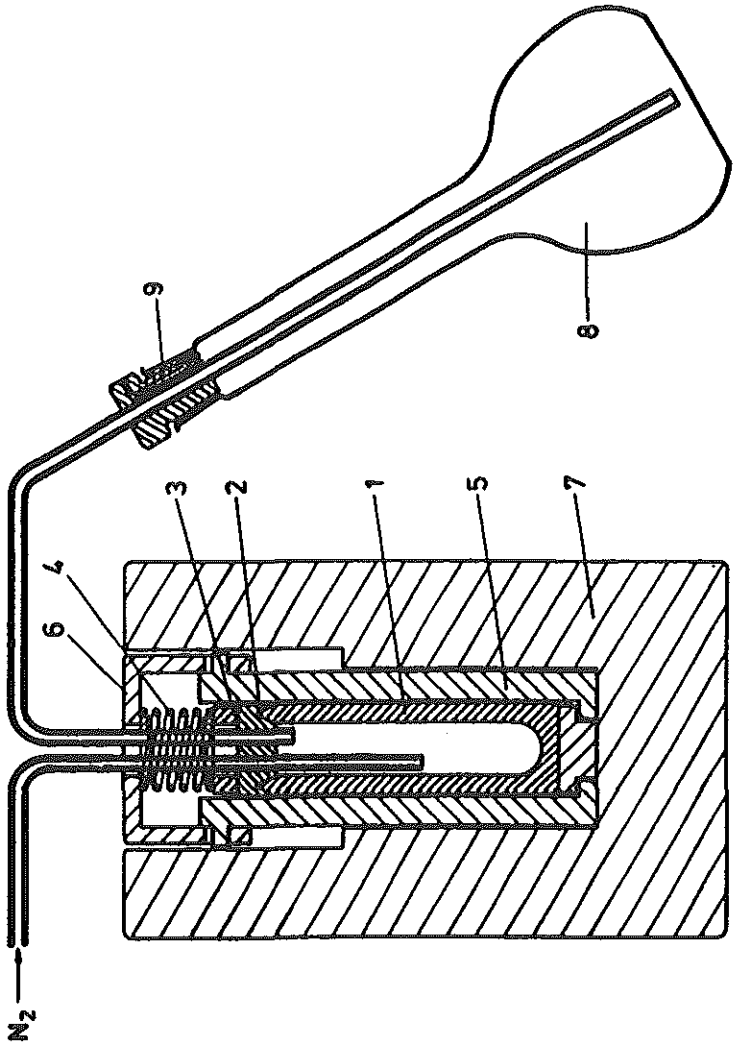
SOURCES of ERROR from MULTI-STAGE procedures

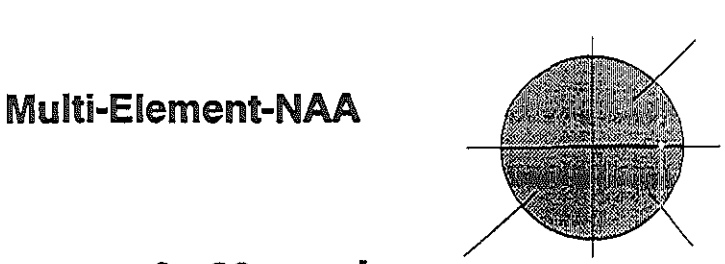



5 cm
1 heating
2 cooling finger
1
2



1 reflux condenser
2 steaming chamber
3 vapour tube
4 overflow
5 round bottomed flask
6 heating


9
8
3
2
1
5
7
4
6
N_2



2 - 20 mg dust

10 - 100 mg dust

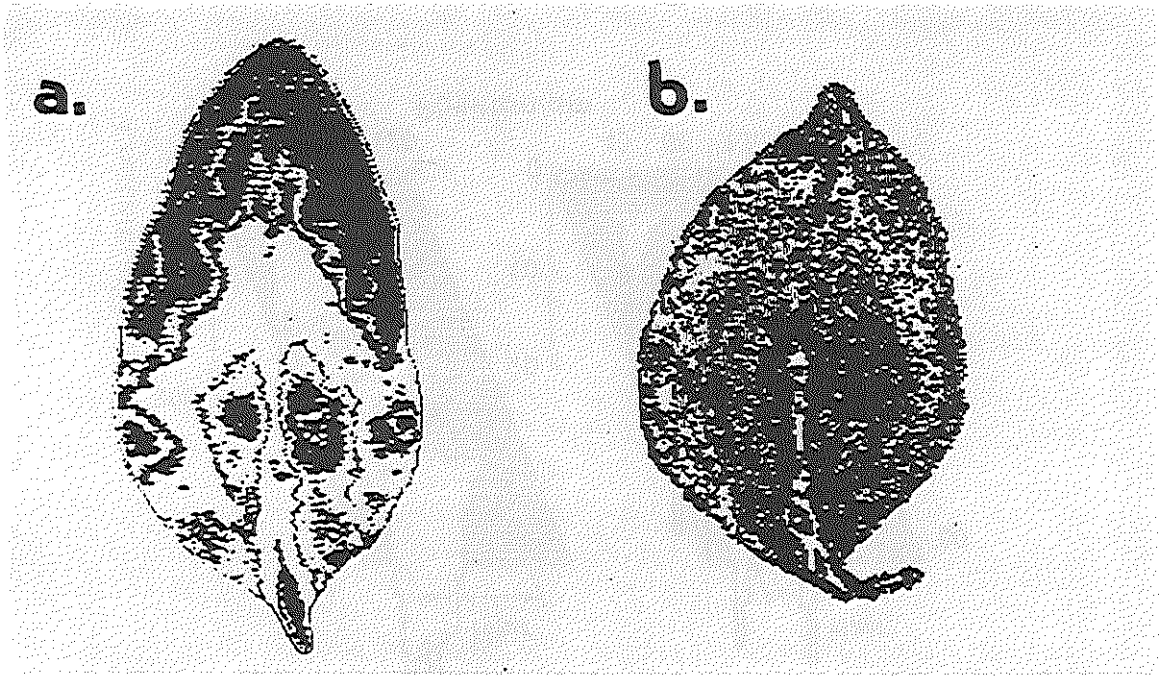
5 min (1 Probe) +1Monitor irradiation (15 Proben) 5 h

20 min | 3 min | cooling | 1 d | 18 d (decay Br-82)

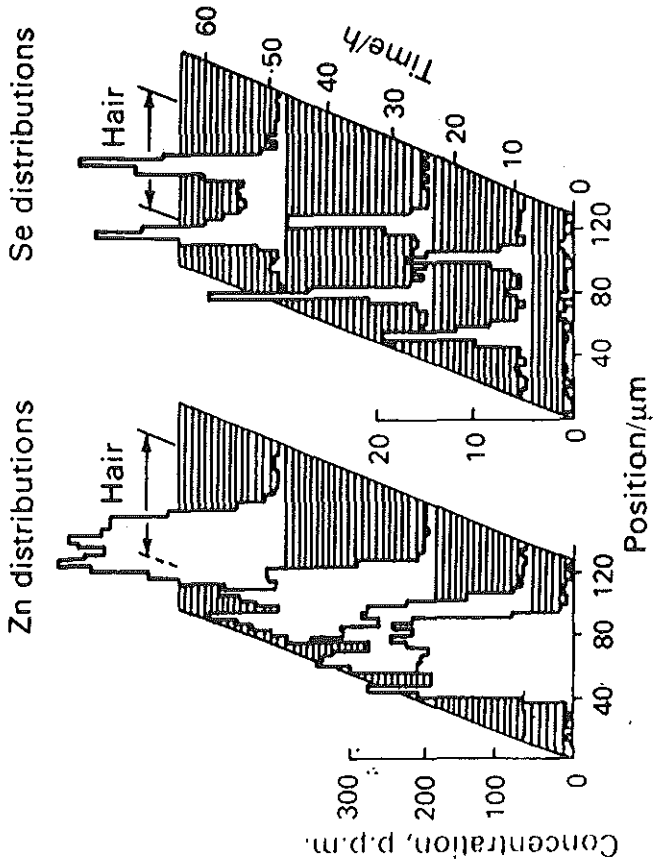
20 min | 6 min | 2 min measurements | 25 min | 100 min

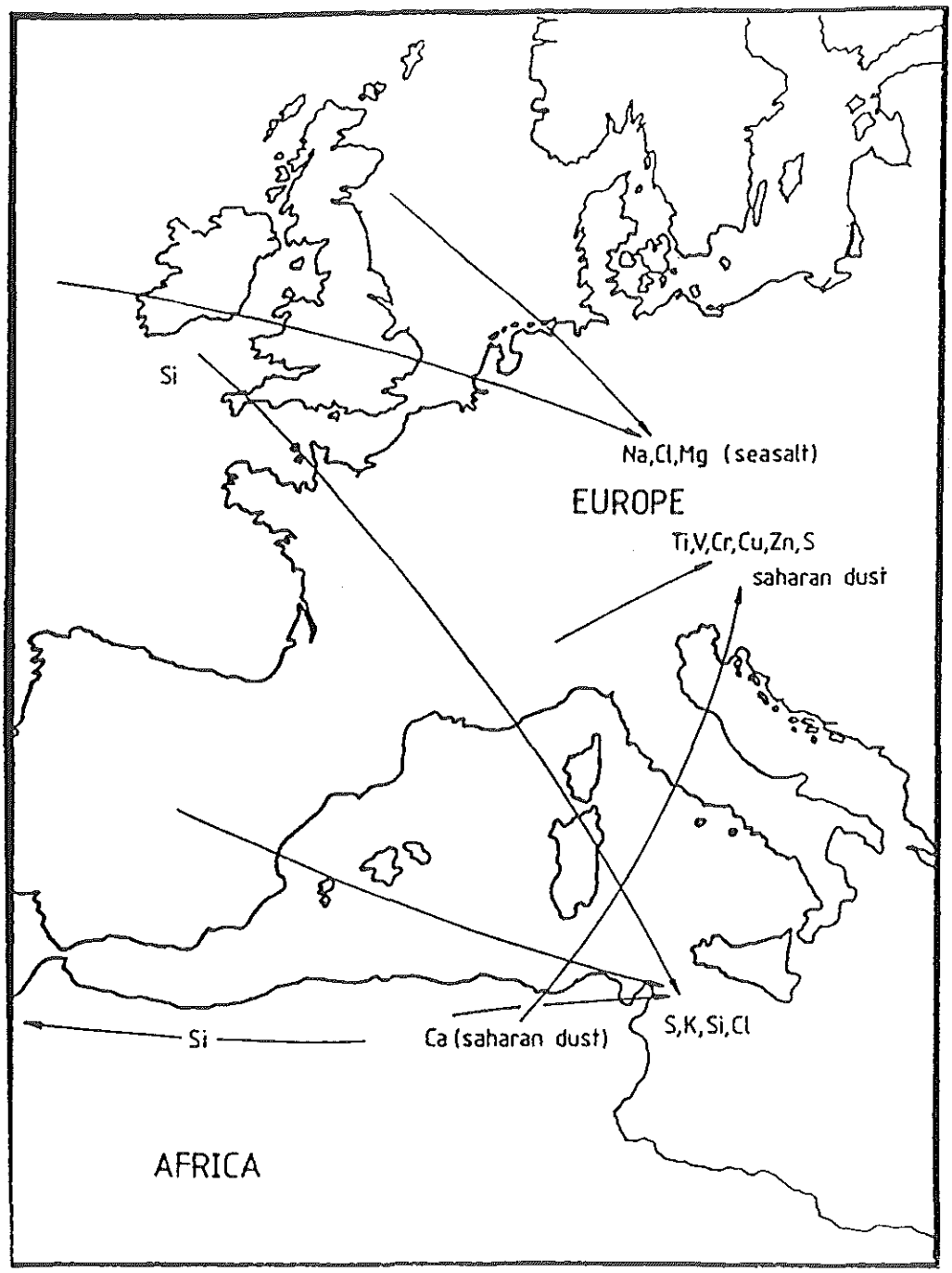
20 min	6 min		25 min	100 min
Na - 24	Al - 28	nuclide	Na - 24	La - 140
Mg - 27	S - 37		K - 42	Sm - 153
Cl - 38	Ca - 49		Cu - 64	Ga - 72
Mn - 56	Ti - 51		Zn - 69m	W - 187
Be - 80	V - 52		As - 76	Eu - 152m
In -116m	Cu - 66		Br - 82	Au - 198
J - 128			Sb - 122	
Dy - 165			Ba - 135m	
Ba - 139				

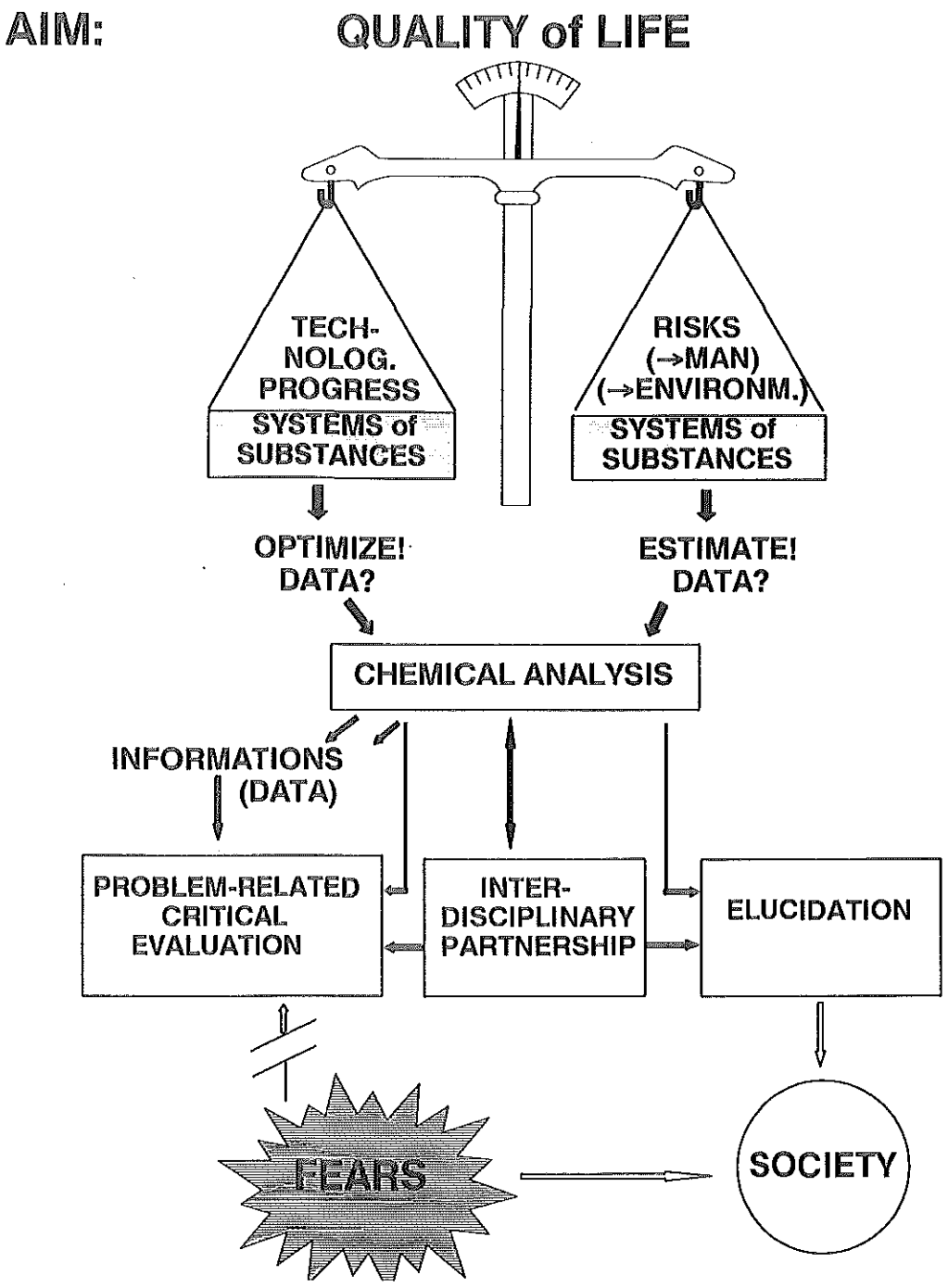
typ. limits of detection 0.01 ... 20 ng/m^3



Manganese distribution in cotton–plant leaf
(a: healthy, b: faded).


Zn distributions
Se distributions
Hair
Hair
Concentration, p.p.m.
300
200
100
0
40
80
120
Position/μm
20
10
0
Time/h
60
50
40
30
20
10
0
40
80
120


Si
Na,Cl,Mg (seasalt)
EUROPE
Ti,V,Cr,Cu,Zn,S
saharan dust
Si
Ca (saharan dust)
S,K,Si,Cl
AFRICA


AIM:
QUALITY of LIFE
TECH-
NOLOG.
PROGRESS
SYSTEMS of
SUBSTANCES
RISKS
(→MAN)
(→ENVIRONM.)
SYSTEMS of
SUBSTANCES
OPTIMIZE!
DATA?
ESTIMATE!
DATA?
CHEMICAL ANALYSIS
INFORMATIONS
(DATA)
PROBLEM-RELATED
CRITICAL
EVALUATION
INTER-
DISCIPLINARY
PARTNERSHIP
ELUCIDATION
FEARS
SOCIETY

relative elemental abundances in magmatic rocks (according to S.R. Taylor, 1964)

		x 10^{-3}		x 10^{-4}		x 10^{-5}	
O	.462	Ti	5.7	Zr	1.6	Ga	1.5
Si	.280	H	1.4	Cl	1.3	Pb	1.2
Al	.082	Mn	1.0	V	1.3	B	1.0
Fe	.056	P	1.0	Cr	1.0	Th	.9
Ca	.041	F	.63	Rb	.9	Pr	.8
Na	.024	Ba	.43	Ni	.7	Sm	.6
Mg	.023	Sr	.37	Zn	.7	Gd	.5
K	.021	S	.26	Ce	.6	Ge	.5
	.989	C	.20	Cu	.5	Hf	.3
			11.0	Y	.3	Dy	.3
				La	.3	Yb	.3
				Nd	.28	Er	.28
				Co	.25	Be	.28
				Sc	.22	U	.27
				Li	.20	Ta	.20
				N	.20	As	.18
				Nb	.20	Mo	.15
					10.6		9.3

Ubiquitous concentration: ca 10 - 500 ng/g Hg

origin		Globally released [t/year]
Natural:		
Volcanism + weathering		500 - 5000
Gaseous from earth's crust		25000 - 15000
Oceaning reservoir: 2 x 10^8 tons		
Evaporation	from sea	23000
	from rivers and glaciers	3800
Anthropogenic:		
Hg - processing industry		6000 - 10000
Processing of ores + minerals		1500 - 20000
Combustion of fuels		100 - 8000

Conclusion on elemental trace anlysis

(1) compendium of instrumental methods available

\+ high power of detection +

\- accuracy requires SRM to compensate for matrix effects -

(2) improve detection power for differentiation

a) of species

b) of microlocal domains

(3) assessment of accuracy

* independent methods approach
* multi-stage procedures
* traceability ⟶ SRM ↓ direct instrumental procedures

Trace metal pollutants in El Manzala lakes by Inductively Coupled Plasma Spectroscopy

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Abstract

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was used to determine a number of toxic heavy metals and other pollutants in the aquatic environment of El Manzala area. Mean and standard deviations are tabulated for lead, cobalt, cupper, cromium, cadmium, zinc, zirconium and strontium determinations in 3 different zones representing the whole area The results indicated several folds increase than those reported for other surface waters in Egypt or in the meditteranean sea shores, with peak valued towards the north part of the lake, west of Port Said city. Zinc and cadmium concentrations are extremly low.

Continual monitoring control of pollutants in surface waters and primary treatment of waste effluents on the waste generation sites are recommended.

Introduction

Several metals occur in rivers and lakes from different domestic and industrial human activities, dead and decomposing animals and vegetation, fallout of atmospheric particulates and from rocks and soils exposed to surface waters (1). Heavy metals are not biodegradable and enter the food chain through a number of pathways causing progressive toxic actions due to the accumulation in different organs over the life span and long term exposure to contaminated environments (2).Despite the presence of trace cocentrations of Cr, Mn, Co, Cu, and Zn in the aquatic environment which is essential to number of life processes; high concentrations of these metals and of several others become toxic (3).

The major water lakes within El Manzala area suffer from uncontrolled disposal of increased amounts of wastes. Effluents from more than 200 sewage disposal units and about 80 industrial facilities pass to El Manzala lake, meanwhile about 1.2 million m3/d of different effluents from the local sewage disposal units are passed to Bahr El Bakar canal. This causes serious environmental pollution in El Dakahlia, El Sharkia and Port Said areas.

This presentation is a part of a programme to monitor the toxic elements and natural radioactivity in the major water resources in Egypt. Several water samples were collected from different governerates within El Manzala area and analysed for Pb, Co, Cu, Cd, Zn, Zr, and Sr. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is used to provide a viable solution for long term environmental control.

Experimental

1. Sampling

Several water samples were collected from different sites within El Dakahlia, El Sharkia and Port Said governerates including the highly populated areas near Port Said and El Mataria cities, Bahr Hados which is a small closed lake south/west of El Manzala lake and from a number of other sites within the lake, as indicated in Fig. (1). These samples were collected by El Manzala lake Department of the general authority for Fish Resources Development, El Dakahlia, clarified by cintrifugation, acidified and kept in polyethylene containers. The following summary presents the main characteristics of the sampling sites and the collected samples.

i- from Bahr Hados site between El Dakahlia and El Sharkia governerates, samples were collected from a heavy muddy area with surface vegetations; at 1.5 m depth, 25°C , brown in color with 20 cm transparency and pH 7.4.

ii- from Bahr El-Bakar site between EL Sharkia and Port Said governerates, samples were collected from a heavy muddy area with surface vegetations; at 2 m depth, 25°C, black in color with 10 cm transparency and pH 7.7.

iii- from Mataria/Port Said canal near Ben Salem between El Dakahlia and Port Said governerates, samples were collected from a heavy muddy area with surface vegetations; at 3 m depth, 20° C green-browinsh colour with 25 cm transparency and pH 7.8.

iv- from Bahr Legan site within El Dakahlia governerate, samples were collected from a sandy mud area at 1.5 m depth, light green in colour with 30 cm transparency and pH 7.7.

v- from Bahr Deshdi site within El Dakahlia governerate, samples were collected from a sandy muddy area at 1.2 m depth, 25°C, light green in colour with 30 cm transparency and pH 7.9.

vi- from the Mataria zone near the population area, samples were collected from a muddy area at 3 m depth, 25°C, light brown in colour with 25 cm transparency and pH 7.8.

vii- from Bahr El-Gamil site near Port Said area, samples were collected from a sandy area at 7 m depth, clear blue, pH 7.3.

2. Instrumentation

The ICP-AES measurements were done with a compact tuned-oscillator with high resolution Echelle grating spectrometer, minicomputer control services, peristaltic pump and an automated sample changer. The system includes a plasma Spec./Leeman 2.5 kw generator with 3-turn copper load coil and a Hidebrand Grid nebulizer.

The spectrometer system is a fixed optics type, f8 Echelle model with single pass prism/lens used for stray light reduction to cover a wavelength range from 190 to 800 nm, 1 PMT for sequential operation

3. Analysis

i-measurements

ICP-measurements were done in the sequential multielement mode. An analytical programme was established both for calibration and routine analysis including a series of automated operations to align the optics, peak the selected analytical wavelengths and position the source image on the entrance slit for signal optimization. The selected analytical wavelengths represent the characteristic lines which are free from spectral interference to elimenate any correction at the concentration levels of interest; these are:

Cr	205.55	(nm)	Cu	324.75	(nm)
Pb	220.35		Cd	214.44	
Co	228.62		Zn	313.86	
Zr	343.82		Sr	407.74	

Measurements were done in triplicate according to the following operating conditions :

forward r.f.power	1.00 KW (0.5 A)
argon flow rate	12 L/min
nebulizer gas	0.3 - 0.5 L/min
sample uptake rate	1 mL/min

ii-standards

The standard solutions were prepared from spec. pure chemicals diluted with D.D demineralized water and adjusted to 0.3 M nitric acid and NaCl was added to coincide with the samples. Mixed working standards containing concentrations proportional to the respective detection limits were prepared by the dilution of the stock solutions for calibration and routine analytical runs.

Results and discussion

The samples analysed were collected from 3 different areas within El Dakahlia and Port Said representing the north, middle and south aquatic environment in El Manzala lake.

The results (table 1) indicate that lead, cobalt, copper and chromium concentrations follow a common distribution behaviour. The metal concentrations increase towards the northern parts of the lake according to the following descending order

$$Pb >> Co > Cu > Cr.$$

Lead is present in the highest concentration levels within the whole area and its concentration ranged from 390 ug/ L in the southern parts to 1650 ug/ L in the northern parts of the lake, west of Port Said city; cobalt ranged from 65 to 250 ug/L copper from 70 to 160 ug /L and chromium from 35 to 100 ug/ L .

These values are several times higher than those reported for most of the Egyptian surface waters (4,5), and even higher than those found around a number of cities on the Mediterranean sea (6 - 8). The high concentration of these pollutants in the northern part of the lake constitute peak values in all cases. This high concentration may be attributed to the clear aquatic environment, absence of surface vegetation, high population density with several human activities, the uncontrolled release of different waste effluents, fisheries and the international navigation nearby the area.

The low concentration of these elements in the southern zone of the lake may be explained by the absorption characteristics of surface vegetation, the availability of considerable quantities of suspended particulates, the muddy nature of the aqueous system, the accumulation of sewage sludge and the nature of the soil in the area. Other physical and chemical processes including change in pH, temperature and the presence of excessive quantites of different organic residues may also contribute in immobilization of several heavy metals (1).

Zinc and zirconium concetrations were found consistent all over the whole area. The concentration of zinc , was extremely lower than the detection limit of the measuring system (<2 ug/L). This seems to be lower by several orders of magnitude than the other values so far reported for most of the surface waters in Egypt (4,5), or in other parts on the mediterranean sea shore (6,9). Zirconium was also measured and its concentration was found almost constant in all the samples and found to be within 45 ug/L as mean value. There is no data available for comparison in similar areas.

Cadmium concentrations were found to be extremely low and

were almost within the ppb range (less than 2 µg/L), however, higher concentration were localised in Bahr Hados (being 20 µg/L) which is a small closed lake south/west of El Manzala lake and in Bahr El-Gamil near the Mediterranean sea, west of port Said (about 10 µg/ L).

Strontium being a member of the alkaline earth elements proved to be present in all samples with high concentrations. In the middle and south aquatic systems of El Manzala lake the concentration levels varied from 1 to 1.8 x 10 µg/L , while in the northern part west of Port Said the mean value was 14.3x10 µg/L . The sandy/lime stone nature in the northern parts of the lake and the absence of suspended particulate and vegetation may be the cause of these high values.

One concludes that the high concentration levels of toxic metals in El-Manzala lake , especially in the northern part west of Port Said (Fig.2), causes considerable pollution in the aquatic environment. This pollution may negatively affect the marine life and accordingly the human beings through the assimulation of polluted sea food. The difficiency of zinc in the area might have a negative biological effect. To minimize environmentatl hazards, the current levels of potentially toxic elements need to be continuously monitored and primary treatment of waste effluents at the sites where toxic metals originate is essential. ICP-AES proved to be a reliable, precise, accurate and efficient method with high sensitivity for the determination of ultra micro quantities of a large number of elements.

Acknowleadgement

The authors acknowledge the effects of Prof.Dr.R.Zaghlol, Head of the Department of Environmental Radioactivity, Hot Laboratory Center, Atomic Energy Authority, Cairo, in providing the water samples.

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Figure captions

Fig. (1) sampling sites
Fig. (2) Concentration levels of metallic pollutants in El Manzala lakes

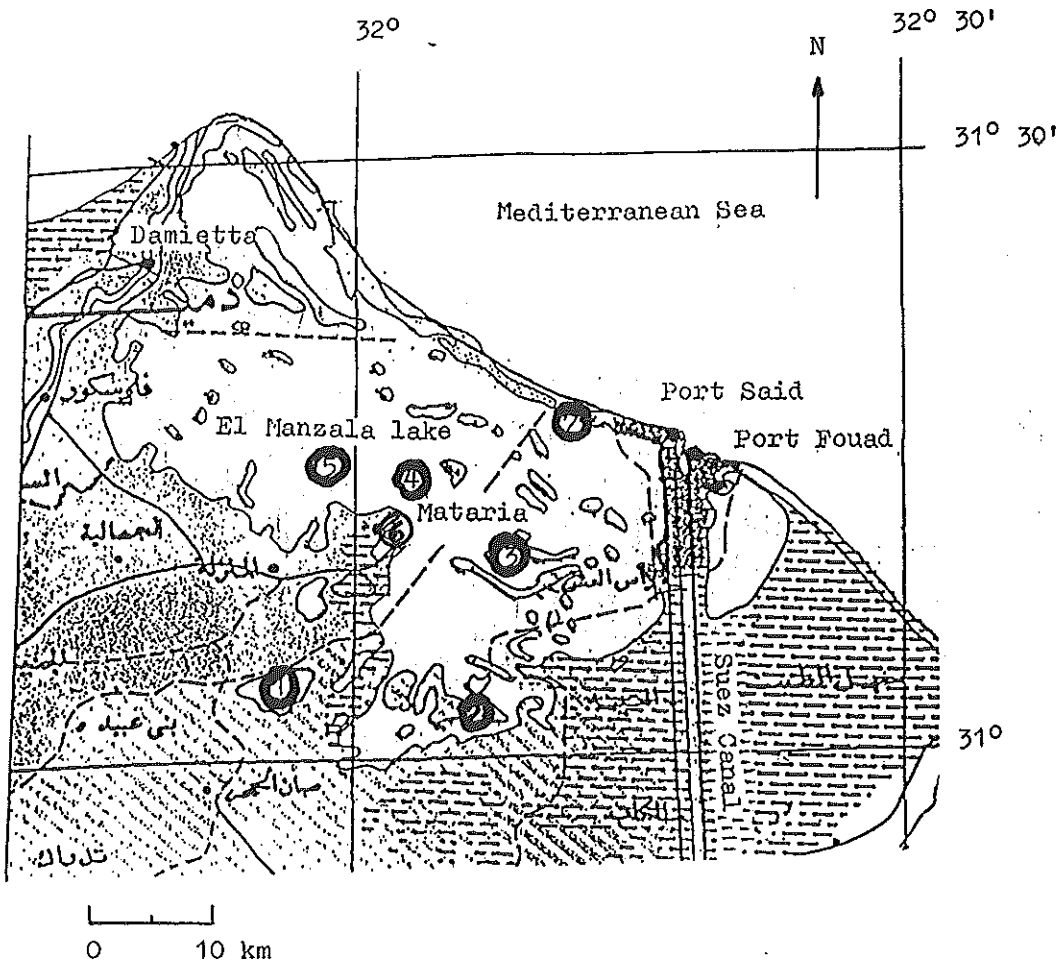

Fig. (1) Sampling sites

1-Bahr Hados
2-Bahr El-Bakar
3-Mataria/Port Said canal (near Ben Salem island)
4-Bahr Legan
5-Bahr Deshdi
6-Mataria zone (near population area)
7-Bahr El-Gamil (near Port Said area)

Fig. (2): **Concentration Levels of Metallic Pollutants in El Manzala Lakes**

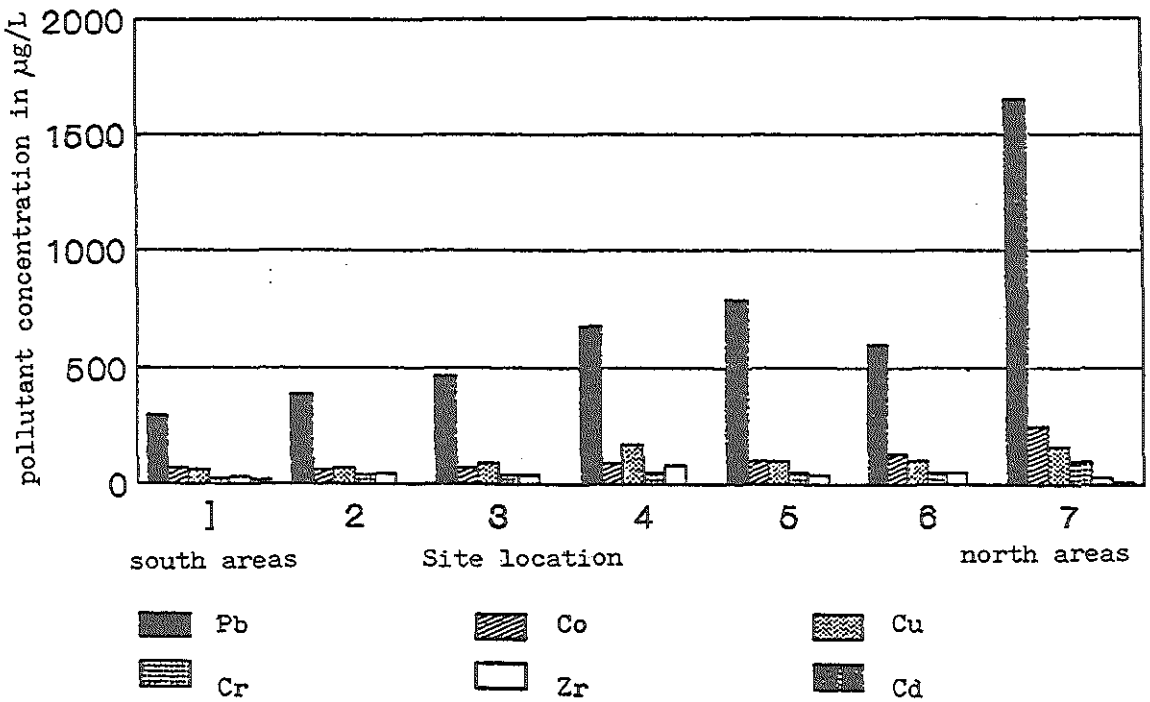

Table (1): Determination of lead and cobalt in El Manzala lakes*)

sampling sites	Pb-concentration,			mean	Co-concentration,			mean
South areas								
1-Bahr Hados	422	246	220	296 ± 109	83	48	71	68 ± 17
2-Bahr El-Bakar	283	577	299	386 ± 164	55	54	79	63 ± 14
3-Mataria/Port Said canal (near Ben Salem island)	358	518	518	465 ± 92	41	78	90	70 ± 25
Middle areas								
4-Bahr Legan	705	625	705	678 ± 46	97	94	88	93 ± 4
5-Bahr Deshdi	870	827	667	788 ± 106	107	94	99	100 ± 6
6-Mataria zone (near population area)	630	715	443	596 ± 139	138	141	114	131 ± 14
North area								
7-Bahr El-Gamil (west Port Said city)	1450	1680	1810	1650 ± 182	251	264	237	251 ± 13

*) lead was measured at wavelength 220.35 nm and cobalt at 228.62 nm; metal concentrations are expressed in µg/L.

Table (2): Determination of copper and chromium in El Manzala lakes*)

sampling sites	Cu-concentration,			mean	Cr-concentration,			mean
South areas								
1-Bahr Hados	54	52	61	55 ± 4	23	29	29	24 ± 3
2-Bahr El-Bakar	57	77	75	70 ± 10	41	40	38	39 ± 1
3-Mataria/Port Said canal (near Ben Salem island)	68	102	91	87 ± 17	46	38	32	39 ± 6
Middle areas								
4-Bahr Legan	147	181	184	171 ± 20	60	48	40	49 ± 9
5-Bahr Deshdi	81	111	111	101 ± 17	60	50	48	53 ± 6
6-Mataria zone (near population area)	93	102	105	100 ± 6	63	47	49	53 ± 8
North area								
7-Bahr El-Gamil (west Port Said city)	199	163	124	162 ± 37	102	101	89	98 ± 7

*) copper was measured at wavelength 324.75 nm and chromium at 205.55 nm; metal concentrations are expressed in µg/L.

Table (3): Determination of zinc,*) zirconium, cadmium and strontium in El Manzala lakes**)

sampling sites	Zr-concentration,			mean	Cd-concentration,			mean	Sr-concentration,			mean
South areas												
1-Bahr Hados	28	28	26	27 ± 1	9	22	41	24 ± 4	1060	1070	1090	1070 ± 10
2-Bahr El-Bakar	38	39	55	44 ± 9	-	1	-	0	1810	1780	1770	1790 ± 20
3-Mataria/Port Said canal (near Ben Salem island)	46	38	45	43 ± 3	2	1	-	1 ± 1	1300	1260	1260	1270 ± 20
Middle areas												
4-Bahr Legan	81	72	77	77 ± 4	1	3	1	2 ± 1	1490	1510	1520	1510 ± 10
5-Bahr Deshdi	38	36	37	37 ± 1	1	2	6	3 ± 2	1410	1450	1450	1430 ± 20
6-Mataria zone (near population area)	41	47	54	47 ± 6	1	-	3	2 ± 1	1410	1410	1410	1410
North area												
7-Bahr El-Gamil (west Port Said city)	18	38	27	26 ± 6	14	14	14	14	14200	14400	14300	14300 ± 90

*) zinc concentrations were found to lie below the detection limit of the system in all samples.
**) zinc was measured at wavelength 313.68 nm, zirconium at 343.82 nm, cadmium at 214.44 nm and strontium at 407.74 nm; metal concentrations are expressed in µg/L.

Table (4): Concentration levels of metallic pollutants in El Manzala lakes*)

sampling sites	Pb	Co	Cu	Cr	Zn	Zr	Cd	Sr
South areas								
1-Bahr Hados	300	70	60	25	b.d	30	20	1070
2-Bahr El-Bakar	390	60	70	40	b.d	45	0	1790
3-Mataria/Port Said canal (near Ben Salem island)	470	70	90	40	b.d	40	0	1270
Middle areas								
4-Bahr Legan	680	90	170	50	b.d	80	0	1510
5-Bahr Deshdi	790	100	100	50	b.d	40	0	1430
6-Mataria zone (near population area)	600	130	100	50	b.d	50	0	1410
North area								
7-Bahr El-Gamil (west Port Said city)	1650	250	160	100	b.d	30	10	14300

*) metal concentrations are expressed in µg/L as mean values of triplicate determinations; zinc concentrations were below the detection limit in all samples.

ASSESSMENT OF POLLUTANTS IN LAKE MANZALA USING GAMMA-RAY SPECTROSCOPY

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**** Nuclear Research Centre, Atomic Energy Authority, Cairo, Egypt.**

INTRODUCTION

A cooperation programme between Egypt and Germany was established to assess the different pollutants in rivers, lakes and soils. These pollutants include both organic and inorganic toxic species. Different techniques are developed for determination of inorganic pollutants among these the use of prompt γ-ray neutron activation analysis technique. In the first phase of this programme, anticompton prompt γ-ray neutron activation analysis system was developed and constructed at the Hot Laboratories Centre. This system is characterized by high resolution, low background, flexibility of the measurements and convenience of the analysis(1).

The second phase of this work is directed to analyse different environmental samples using the developed PGNAA system. A first candidate to apply this analytical technique is Lake Manzala. This lake is located in North Egypt and west the Nile Delta. The water in this lake suffer from uncontrolled disposal of effluents from more than 200 sewage disposal units and about 80 industrial facilities. This bring serious environmental pollution in the water of the different Governerate located around the lake.

In this contribution, several water samples from lake Manzala were collected and analysed for different elements by the PGNAA technique. Some measurements from lake Karon were also given for comparison.

EXPERIMENTAL

Different water samples were collected from lake Manzala. The samples were collected by the El Manzala Lake Department of the General Authority for Fish Resources Development, El-Dakahlia. The water samples were clarified by centrifugation, acidified and then kept in polyethylene bottles.

The PGNAA system was described previously (1). It is based on activation of the samples with Cf-252 neutron source (original activity of 740 MBq give a flux of 1.5 x 10^8n $cm^{-2}.S^{-1}$) and measurement of the prompt gamma rays with anticomption system using high purity Ge detector. The system is designed to give high efficiency and low background. The different elements were identified is based on the expected prompt gamma energy and given in Table (1). The irradiation time was generally five hours and the results obtained after corrections. Quantitative analysis is based on comparison with reference materials obtained from IAEA.

RESULTS AND DISCUSSION

In this work, the preliminary results of this programme will be reported. Figure 1, is a typical prompt gamma spectrum of 50 ml of Manzala lake water measured in polyethylene bottle during irradiation by the given Cf-252 neutron source for five hours. Figure (2) shows a similar spectrum for water sample from lake Karon.

From these Figures, it clear that the water sample contains mainly Cd,Ir, In and, the lanthanide elements Pr, Nd, Sm and Gd. Presence of the lanthanides elements is explained in terms of the Monazite deposits on the Egyptian Meditereanion shore. It is well known that Monazite contains several lanthanides. As for heavy metals, Cd and In seems to be the main pollutants in the samples studied. Quantitative analysis was carried out for Cd, Gd and Sm in different samples from Manzala lake, Table (2).

Analyses were based on the gamma- spectrum for each sample . Seven water samples from Manzala lake, 3 water samples from lake Karon and 7 rock samples form the region. These results represent the first from expanded programme to cover different elements for both anions and cations. Comparison with other anaytical techniques will be considered for assessment and verification of the results

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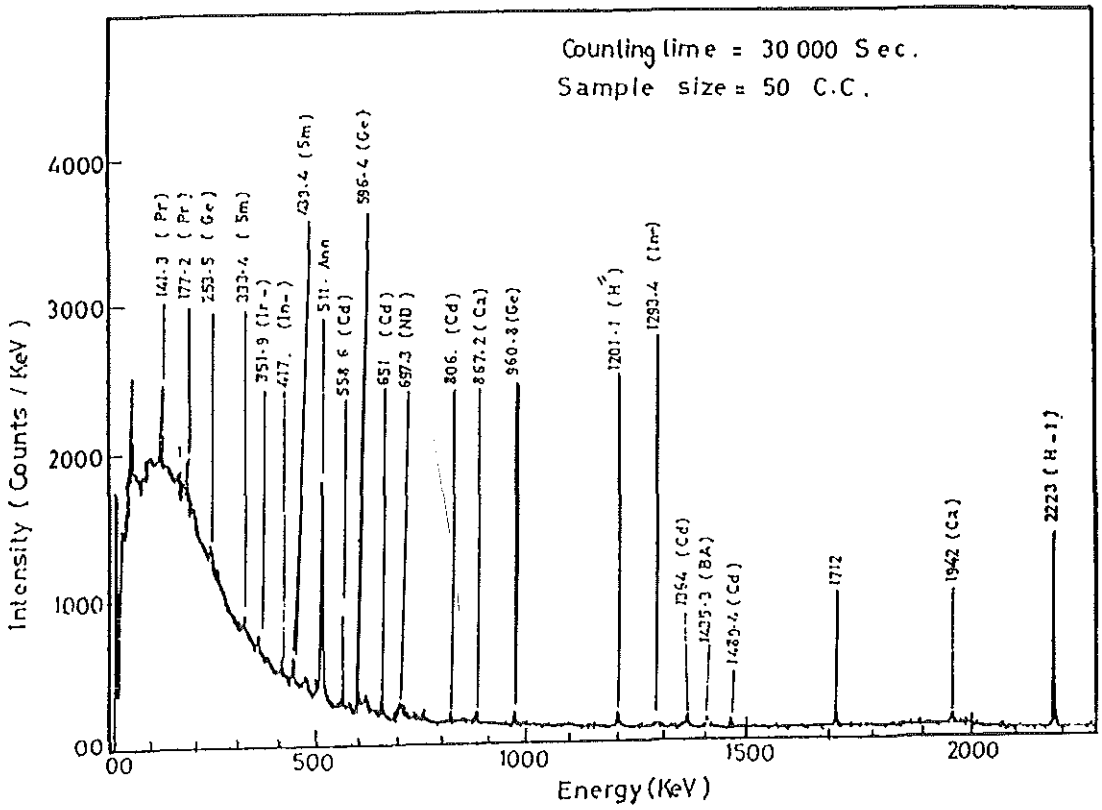

Fig.(1): Anticompton prompt neutron gamma-ray spectrum of water sample of local Manzala lake

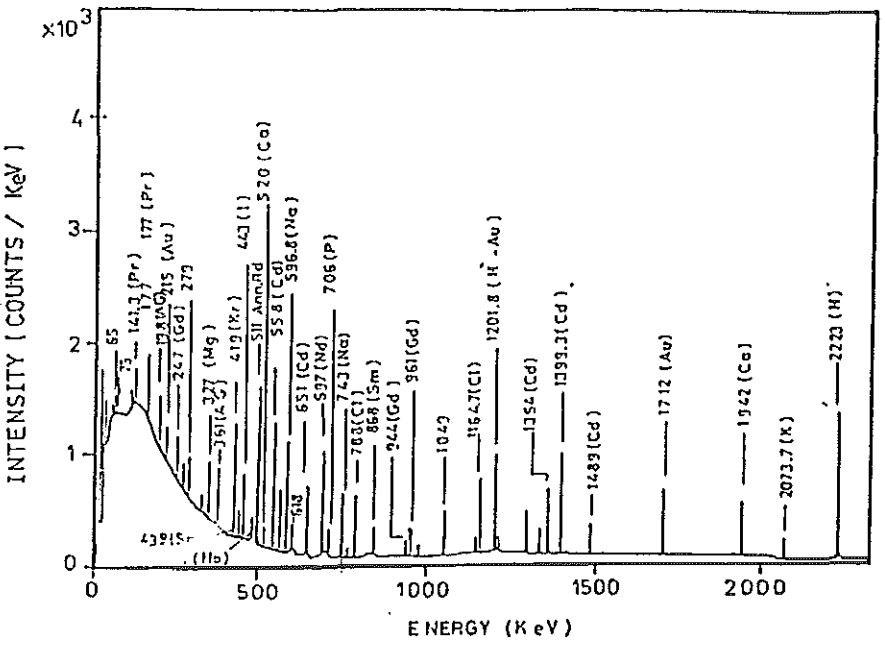

Fig.(2) Anticoincidence spectrum of water sample, of Karon lake (EL-Fayum).

Table (1)

Identified elements and its neutron capture gamma-ray energies in Manzala-lake water sample.

Element	Energy (KeV)
Ca	520, 726.9, 1942
K	1461, 770.2
Na	472.4, 870.6
Cl	1164, 1618, 1942
Ba	627.5, 1435
Ir	351.0,
Ge	500.2, 3028
Pr	141.2, 177.2, 4801
Mn	7058
In	1097, 1293.5, 417.7
Cu	6575., 7252., 466.0
Co	320.0, 5659
Sm	333.4, 439.4, 868.
Cd	558.5, 806.,
Zn	6655, 6910
Gd	199., 961.8,
Pb	6736, 7367.7
I	133.6
Ti	341.8, 983.4, 1381.7
Si	1273.3, 3539., 4934
Au	1201.8, 2458.9, 5103, 5394

Table(2)

Quantitiative analysis for Cd,Gd and Sm in some analysed sample (by ppm)

Sample	Cd	Gd	Sm
*M-1	< 5	6	< 5
M-2	< 5	6	< 5
M-3	< 5	8	< 5
M-4	27	42	35
M-5	40	35	44
M-6	< 6	< 5	< 5
M-7	52	6	8
*K-4	67	9	10
K-10	69	14	13
K-18	72	25	14
*R-1	45	10	8
R-2	40	25	6
R-[illegible]	80	50	15
R-10	90	65	48
R-25	95	70	55
R-31	100	35	83
R-32	38	30	7
*B.S.sample	128	110	85

* M : Manzala-lake sample
* K : Karon-lake sample
* R : Rock-sample
* B.S: Black-sand sample.

ENVIRONMENTAL SPECIMEN BANK OF THE FEDERAL REPUBLIC OF GERMANY
- SIGNIFICANCE OF SURFACTANTS -

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Summary

Environmental contaminants in water, soil and air as well as changes in their concentration with respect to space and time may be quite effectively detected by the analysis of appropriate indicators (biomatrices from different levels of the food chain, sediments, sludges, dusts) which accumulate these chemicals by several orders of magnitude.

However, regular monitoring of the environment should not be restricted to presently known substances. The suitable storage of representative indicator specimens allows also the retrospective analysis of chemicals which are not detectable at present or which have not been regarded as environmental pollutants so far.

Therefore, the German Environmental Specimen Bank (ESB) of the Federal Government was established in 1985 with the purpose of storing representative samples from the terrestrial and aquatic environment as well as from human beings for future decades without any change in chemical composition.

In spite of its relatively limited time of operation, the ESB has already obtained a variety of promising results which support not only the success of legislative regulations (introduction of unleaded fuels, ban on pentachlorophenol) but demonstrate also the decrease of pollutants in rivers due to reduced industrial or municipal discharges. Moreover, the effectivity of new technologies with respect to environmental protection may be traced back by a specific and retrospective characterization of suitable indicator samples.

In addition to its routine programme, the Institute of Applied Physical Chemistry of the Research Centre Jülich (KFA) is performing basic studies on the speciation of selected elements such as arsenic, mercury and tin, and the determination of new compounds. In this respect, surfactants play an important role because they can influence the immobilization or remobilization of pollutants in soils or sediments. The mobility of other chemicals in such

matrices can be estimated, if surfactant concentrations are known. With that, a prediction of possible contaminations of ground or surface waters is possible. Selected examples will be discussed in detail in the following.

Introduction

One of the most urgent tasks of the environmental protection policy consists in the regular monitoring of pollutants in water, soil and air, as well as in various stages of important food chains (plants, animals), finally leading to man. However, this monitoring should not be restricted to the determination of stationary pollutant loads. On the contrary, it requires in particular information about their time- and space-dependent behaviour under natural environmental conditions. Therefore, the following questions should be answered as a first priority:

- Where do these materials persist and where do they possibly accumulate?
- What chemical form are they present in?
- How mobile are they in the environment?
- Why are they mobilized or immobilized?
- What short- or long-time effect do they have on man and the environment?
- When and how do new pollutants appear in the environment?
- What new substances are environmental chemicals converted into and in what time?
- Do toxic substances - possibly - result during this process and how stable are they?

With the knowledge and methods previously available, possible influences and impacts of the environmental chemicals produced by man and intentionally or unintentionally released into the environment on natural or semi-natural ecosystems, and also on the basic necessities of life and the health of mankind can only be inadequately forecast or their potential dangers assessed [1].

According to the "European Inventory of Existing Commercial Substances" **EINECS** (after GDCh/BUA) [2], there are currently approx. 100 000 different chemical substances whose behaviour and action in the environment are still largely unknown [3].

It is therefore all the more important that even the smallest changes in the environment and in the various trophic stages and food chains should be detected by specific observation and monitoring. Their origins have to be elucidated and if necessary their further development should be halted. Corresponding scientific and technical activities place particular emphasis on the protection of mankind and the environment against anthropogenic and geogenic pollutants,

as well as their systematic and continuous detection in soil, water, air and selected biological specimens.

On the basis of their specific accumulation potential for certain pollutants, biological samples have the advantage that changes in the local or regional pollution situation can be recognized much more easily. They thus have a special indicator function in the determination of pollutant trends or the early recognition of new chemicals in the environment (see Fig. 1).

Tasks of the Environmental Specimen Bank

The characterization and evaluation of environmental and human samples - in their **actual state**, but also in their development over time - creates important prerequisites within the framework of a precautionary policy for the following:

- recognition of impending undesirable developments,
- estimation of nature and extent of undesirable developments already in evidence and their consequences,
- obtaining insights to set priorities for political activities and
- compiling basic principles for the precautionary policy of the Federal Government in the field of nature conservation and environmental protection and also for human health.

As early as 1973, these insights led to the development of a strategic concept of providing the necessary scientific basis for realizing this precautionary policy by establishing an environmental specimen bank. Special guidelines (Standard Operation Procedures, SOP) were developed for all the operating steps necessary for implementation including the analytical work [4].

The long-term usefulness of the stored samples, particularly for retrospective analysis, is ensured by the fact that all materials are deep frozen at temperatures below -150°C immediately after collection. In this way any possible changes in chemical composition are completely prevented or reduced to a minimum [5, 6]. Further sample treatment (processing, homogenization and aliquotization into standardized sub samples) (see Fig. 2) is similarly carried out in the above mentioned temperature range, and strict compliance with these conditions is monitored by continuous controls.

After preliminary analytical studies in 1976 - 1978, the *logistic* and *technical* prerequisites for the feasibility of an environmental specimen bank were thoroughly investigated between 1979

and 1984 in the "Environmental Specimen Bank" pilot project "Environmental Specimen Bank" financed by the BMFT (Federal Ministry for Research and Technology) [7].

Participating Institutions

Since January 1st, 1985 the Environmental Specimen Bank has been established as a permanent institution under the responsibility of the BMI (later the **BMU, Federal Ministry for the Environment, Nature Conservation and Reactor Safety**). The **Federal Environmental Agency (UBA)** is responsible for co-ordination. Two specimen banks are subsumed under the general heading of the **German Environmental Specimen Bank:**

- the **Specimen Bank for Environmental Specimens** - at the Institute of Applied Physical Chemistry of the Research Centre Jülich (KFA) and
- the **Specimen Bank for Human Organ Specimens** - at the Institute of Pharmacology and Toxicology of the University of Münster.

These institutes also take part in the specimen characterization by analyzing heavy metals, metalloids and essential elements in environmental samples at the Research Centre Jülich, whereas the corresponding activities at Münster comprise both the inorganic and also the organic (primarily chlorinated hydrocarbons) analysis.

Furthermore, the work of the Environmental Specimen Bank in the field of ecology and also in the selection of representative areas and specimen species is supported and guided by

- **The Institute of Biogeography at the University of the Saarland.**
- **The Institute of Ecological Chemistry at the GSF Neuherberg** and
- **the Biochemical Institute for Environmental Carcinogens, Grosshansdorf,**

are responsible for the analysis of organochlorine compounds and polycyclic aromatic hydrocarbons (PAH) in the stored terrestrial and aquatic environmental samples (see Fig. 3).

Representatively Selected Ecosystems

With the operation of the German Environmental Specimen Bank [8, 9, 10] as part of the environmental monitoring and ecosystem research network currently in the process of development biological objects in the context of their ecosystem will be preferentially observed

now in addition to the monitoring of air and water which exists already. An overall concept has been developed for this monitoring and thus also for the environmental specimen bank by a committee of experts under the auspices of the BMU, taking into consideration different types of ecosystems with corresponding representative sampling areas. In these areas (see Fig. 4) continuous sampling has been carried out to some extent since 1985, as yet every two years. But this should be converted into a one-year sampling frequency in accordance with an overall concept to be realized by the year 2000 in order to utilize the analytical, biometric and meteorological data much more effectively in the sense of real-time monitoring. Since the unification of the two German states in 1989, representative areas in the former East Germany have also been increasingly studied with the support of local institutions.

Representative Specimen Species

The selection and assignment of representative specimen species from the terrestrial and aquatic environment, and also from the human field, for the specimen bank was similarly undertaken by a committee of experts. This selection is regularly reviewed on the basis of new insights and, if necessary, corrected. However, very serious reasons would be required to eliminate a specimen species that had been collected and stored for a considerable period. At present, the following specimen species are collected on a routine basis:

- from the ***terrestrial*** field: soil samples, tree samples (leaves and shoots), and animal samples (pigeons' eggs, roe deer liver, earthworms);
- from the ***limnic*** field: sediments, fish (muscle and liver), and freshwater mussels;
- from the ***marine*** environment: sediments, algae, mussels, fish (muscle and liver), and sea bird eggs (see Fig. 5).

The specimen species from the ***human field*** (fatty tissue, liver, kidney, blood, urine, hair, saliva) are stored in the specimen bank for human organ samples at the University of Münster. The range of analyzed elements and organic pollutants (cf. p. 6) is largely identical with that of the environmental specimens in order to detect any possible connections between the pollution situation in man and his immediate environment.

As part of supplementary research and development work at the Institute of Applied Physical Chemistry, investigations are currently been carried out - in addition to the routine analytical work - on materials of the environmental specimen bank with the objective of clarifying the possible influences of surface-active substances (surfactants) on the transport behaviour and bioavailability of inorganic and organic environmental chemicals in soils and sediments.

Particular attention is being paid to the determination of synergistic or antagonistic effects as well as questions of the immobilization (bound residues) and remobilization of pollutants.

Results

Terrestrial Environment - Atmospheric Input

The initial characterization of environmental specimens from the terrestrial environment - with four complete data sets to date - as well as the regular examinations of human blood from selected parent populations carried out at six-monthly intervals has already led to reliable and thus credible results about the ubiquitous decrease in lead pollution. Making use of the Institute's own measuring network to determine pollutant deposition by precipitation, it can be demonstrated without doubt that the legal measures to reduce lead emissions (introduction of unleaded fuels in 1984) have achieved significant success. The data collections carried out continuously since 1980 - with weekly sampling - indicate, for example, that in rural regions close to industrial centres lead deposition decreased by more than 70 % in 1992 in comparison to 1980. A comparable trend is apparent in so-called "background regions", not directly polluted, in which wet lead deposition can be almost exclusively attributed to atmospheric long-distance transport (see Fig. 6).

The tree specimens (spruce shoots, beech leaves) collected and stored since 1985 from the regions of the environmental specimen bank also provide convincing documentation of the decrease in lead pollution (see Fig. 6). The same is also true of the human field, as confirmed by the results of the continuous lead studies of blood from student populations at the University of Münster. On the whole, the results provide clear evidence of the positive effects of the introduction of unleaded fuels.

Cadmium contents in tree specimens (leaves, needles) from various regions display higher concentrations at an agricultural site than in an urban industrialized area. Since the plant uptake of this element essentially takes place via the roots, it must be assumed that the different contents depend on the bioavailability or mobility of this heavy metal in the soil.

The reasons for varying bioavailability are very complex and extensive site-related studies are necessary to clarify them. For example, differences in humus content or permanent soil moisture are conceivable. A further possibility results from soil acidification caused by acidic rain. However, ubiquitously occurring surface-active substances (surfactants) should also be taken into consideration with respect to a change in mobility. It was thus demonstrated in

laboratory experiments that cationic surfactants are basically capable of releasing both essential trace elements (Ca^{2+}, Mg^{2+}, Na^{+}) as well as toxic heavy metals (Cd^{2+}) from degraded loess soil (orthic luvisol - approx. 25 % clay mineral fraction). Furthermore, investigations on the clay mineral montmorillonite demonstrated that this release of cations occurs quantitatively and stoichiometrically [11]. In Fig.7 this change in the balance of nutrients and trace elements is demonstrated by the example of a layer silicate loaded with Na^{+}/Cd^{2+}. The addition of the cationic surfactant initially leads to the replacement of relatively weakly bound Na^{+} ions. Only after this displacement process has been completed a quantitative release of Cd^{2+} into the soil solution takes place. But when the monovalent Na^{+} ion is replaced by divalent, essential cations (e.g. Ca^{2+}) in the silicate layer, a simultaneous displacement by the cationic surfactant takes place because both Ca^{2+} and also Cd^{2+} are bound to the exchange sites with comparable strength [11].

Limnic Environment - Inputs into River Water Systems

Considerable pollution with heavy metals and chlorinated hydrocarbons was detected in sediments from the River Elbe collected in 1991 and 1992 in co-operation with the Federal Hydrology Agency (BfG, Berlin office). Thus for example, the salt contents and also the concentrations of some heavy metals such as mercury, cadmium, lead and chromium are extremely high in the region of the Saale estuary. Even if the sediment samples from 1992 display declining mercury concentrations for almost all sampling sites, nevertheless the drastic rise in the region of the Saale estuary (Barby site) is alarming (see Fig. 8).

Likewise, investigations of the Elbe sediments collected in 1991 for chlorinated hydrocarbons and dioxins point to particular pollution problems [12]. However, since these surveys have only recently been included in the analytical programme, reliable conclusions about the time sequence and origin of this pollution can only be obtained by the retrospective analysis of corresponding stored samples.

The convention concluded by the **International Commission for the Protection of the Elbe (IKSE)**, the closure of industrial plants and the improvement in quality of municipal sewage in the upper regions of the Elbe and its tributaries will undoubtedly lead in future to an improvement of water quality particularly in this region. The same expectations can also be placed in the extension of new environmental technologies. In the same way, an experimental verification of this forecast can only be obtained from a retrospective analysis of different sample types from the Environmental Specimen Bank, for example sediment, freshwater mussels and fish (bream).

In contrast to the systematic investigations of the Elbe, which have started only recently, surface sediments from the Rhine have already been analyzed by the Institute of Applied Physical Chemistry since 1978. Samples taken at the Emmerich border station demonstrate a clear reduction in lead and cadmium pollution from 1978 to 1990 (see Fig. 9). The effects of the convention concluded by the **International Commission for the Protection of the Rhine** (IKSR) are particularly apparent here in the same way as the decline in the biological oxygen demand (BOD_5) or the rise in the oxygen concentration, which is one reason for a clear increase in the variety of fish species in the Rhine [13].

As part of the continuous expansion of the range of elements characterized in the initial analysis, the thallium concentration in various limnic samples has been determined for some time. The comparison of current data for bream muscle from two different sampling areas (Rhine/Lake Constance and lake land district of Bornhöved, Schleswig-Holstein) show that the thallium contents of the samples from Lake Constance are higher than the reference samples from the North German area by approximately a factor of 8 (see Fig. 10). More detailed investigations of stored material from the past eight years (retrospective monitoring) furthermore revealed that this is a permanent, excessive pollution of Lake Constance. An acute thallium contamination, initially assumed, can thus be ruled out.

Surface-active substances, in particular cationic surfactants and also the metabolites of the alkyl phenol ethoxylates, possibly also have certain toxic (environmentally toxic) effects in the aquatic environment (surface sediments from rivers, lakes and estuary regions) in the same way as in the terrestrial field. It may also be assumed that a remobilization of heavy metals becomes possible here under the influence of surfactants and thus additional quantitites of these elements become available for bioaccumulation in the various organisms of the limnic or marine food chains.

Marine Environment - Impacts on Estuary and Coastal Areas

Both sea water and also sediment analyses have as yet only rarely been implemented with respect to the biological availability of pollutants. However, since only the available pollutant fraction has toxicological relevance and therefore causes "**pollution**", it is necessary to use increasingly biological indicators to monitor the pollution and pollution capacity of surface waters.

The special significance of such indicators consists in their accumulation potential, which is described in the literature for various marine organisms [14] (see Fig. 1 and 11). For this reason, mainly sediments, brown algae, common mussels, fish (viviparous eelpout) and herring gull eggs are investigated within the framework of the Environmental Specimen Bank programme to characterize a marine sampling area. It is planned to sample seal organs (muscle, fatty tissue, liver) as the final link in the marine food chain.

Brown algae (bladder wrack) and common mussels from the same sampling site display quite different accumulation behaviour with respect to certain elements. As shown in Fig. 12, As, Ba, Mn, S and Zn are, for example, preferentially accumulated in bladder wrack whereas an increased accumulation of Cu, Fe and Hg is found in common edible mussels. Furthermore, significant deviations arise for both sample species in a comparison of the North Sea and Baltic Sea (see Fig. 12), which differ considerably in their salt content. Both North Sea specimens conform in displaying a higher accumulation potential for As and Hg, whereas Ba, Mn and Zn are accumulated to a greater extent in the Baltic Sea specimens. No site-specific allocations of this kind can be made for Cu, Fe and S. On the whole, apart from the matrix-dependent parameters, in particular the salinity and the temperature seem to play a certain part here. Thus, for example, in the literature a relationship is described in certain marine organisms between increased cadmium uptake at high temperature and low salinity [15].

A clear decline in mercury pollution in the estuary region of the Elbe in the past few years can be documented on the basis of samples of herring gull eggs collected in the "Trischen" bird sanctuary and in which up to more than 90 % of the mercury was present in the form of the highly toxic methyl mercury. In comparison to the period before unification of the two German states (1988/89) a reduction in pollution to less than half can be determined for the subsequent years 1990/91/92 (see Fig. 13). Similar results are also shown by an investigation of polychlorinated biphenyls (PCB) [12]. These findings are very probably associated with the closure of industrial plants and municipal sewage disposal in the upper regions of the Elbe and its tributaries. On the other hand, the reduced run-off of the Elbe in the past few years of low rainfall may also have contributed to these results. This urgently requires continuous investigations in the coming years to monitor the new environmental technologies coming into operation, in which connection realistic and reliable statements about the development of the pollution situation can undoubtedly be made only by a systematic, retrospective comparison with past samples.

Due to the sedentary habits of this species, the determination of the mercury concentration in herring gull eggs also permits a clear distinction between adjacent sampling areas with different degrees of pollution. Thus, for example, samples from the bird sanctuary of "Mellum" (Weser

estuary) display considerably lower mercury contents than herring gull eggs from the bird sanctuary of "Trischen" (Elbe estuary) (see Fig. 13).

Additional Research Activities

Apart from continuous monitoring of known pollutants and operation of the Environmental Specimen Bank, the tasks of prognostic environmental precautions also include in particular the investigation of chemicals which, according to the present state of knowledge, do not cause any direct ecotoxicological effects, but whose environmental impacts or possible effects on man and the environment by synergistic or antagonistic effects are as yet completely unknown.

The Institute of Applied Physical Chemistry is therefore involved in investigating those substances which, due to their surface-active properties, may cause an immobilization, remobilization or change of mobility of pollutants - heavy metals and organic substances such as polychlorinated biphenyls (PCB), PAH's or pesticides. The possible surfactant-induced remobilization of pollutants fixed in a "sink" (soils, sediments) is of particular importance here since this would make bound residues biologically available again for plant or animal organisms.

Surface-active substances alter the properties of soil minerals (e.g. layer silicates) by adsorption and hydrophobization of the surface. Even slight quantities of surfactants cause significant effects with respect to the transport and biological availability of pollutants in soils and sediments [16]. This may result in the accumulation of pollutants in the trophic stages of the food chain and the elimination of essential trace elements. Cationic surfactants, for example, cause a drastic alteration in the electrolyte equilibrium between the soil and soil solution due to ion exchange. Both essential cations (Ca^{2+}, Mg^{2+}, Na^{+}) as well as toxic heavy metal ions (e.g. Cd^{2+}) are quantitatively displaced [11].

Hydrophobization of the surface causes basic changes in the adsorption properties of the soil minerals. Neutral (hydrophobic) molecules may be taken up into the surfactant layer. On the basis of this knowledge, alkyl ammonium montmorillonites are being investigated and recommended for sealing landfill sites [17, 18]. Similar sorption processes may take place in soils and sediments. Probably, the hydrophobic character of soil minerals will increase due to the accumulation of surfactants thus promoting the adsorption of non polar less water-soluble substances. That would immobilize them and exclude them from further natural transport or degradation processes.

The following examples are therefore concerned with the impact of surfactants on the interaction between environmental chemicals and the most active clay mineral components (montmorillonite, illite) of the mineral soil horizon or the natural soil structures (e.g. degraded loess soil). Firstly the influence of surfactants on non-essential elements will be discussed. In examining the interactions of organic substances with surface-active substances, the examples are oriented towards the three surfactant classes in the sequence: cationic, non-ionic and anionic surfactants. Details of the materials and analytical methods used, as well as the nomenclature, are described in the literature [11, 19, 20].

Surfactant Interactions with Inorganic Pollutants

The influence of various classes of surfactants on the transport behaviour of Cd^{2+} in degraded loess soil (B horizon) is shown in Fig. 14 [21]. It is apparent that only cationic surfactants are capable of mobilizing sorbed Cd^{2+} by an ion exchange mechanism, in the course of which the surfactants are quantitatively bound to the mineral surface and are not detectable in the equilibrium solution. Non-ionic surfactants (e.g. Triton X 100) are adsorbed much more weakly on degraded loess soil, which may be attributed partially to the van der Waals forces. Accordingly, no Cd^{2+} mobilization takes place. Anionic surfactants form an only slightly soluble salt with Cd^{2+}, namely $Cd(DS)_2$. Therefore, Cd^{2+} immobilization occurs due to precipitation.

Surfactant Influences on Organic Pollutants

Cationic Surfactants

In principle, the adsorption of organic environmental chemicals on layer silicates proceeds extremely slowly so that it may take several weeks to establish an equilibrium state [22]. In contrast, if the layer silicate surface is coated with cationic surfactants in different quantities [22] or of different hydrophobicity, e.g. with DTAB (dodecyl trimethyl ammonium bromide) or DDDMAB (didodecyl dimethyl ammonium bromide) [23] then equilibrium in both systems is reached within 30 minutes, i.e. a drastic increase in the adsorption rate of organic pollutants results. Their residence time or probability of residence in the soil electrolyte is therefore drastically reduced and their bioavailability thus also drops.

Fig. 15 shows the influence of added surfactants on the equilibrium states in the form of adsorption isotherms for 2-naphthol. In this concentration range the isotherms can be described by straight lines, which points to a constant distribution of the naphthol between the solid and liquid phases [22, 24]. Its adsorption rises with increasing surfactant coverage - relative to the

cation exchange capacity (CEC) - until the exchange capacity has been reached. With the addition of even higher quantities of surfactant (600 % of the CEC), the adsorbed amount of 2-naphthol declines again considerably. Micelles are formed in the solution which then compete with the adsorbed surfactant films for the pollutant molecules, which leads to a decrease in the incorporated, adsorbed pollutants molecules (soil washing effect) [22].

Detailed information about the binding site of the organic compounds and the structure of the adsorbate layer can be obtained by X-ray diffractometry. For example, nitrophenols are intercalated in the inter layers of the swellable, hydrophobed bentonites [23], which may essentially influence their further fate (transport, degradation behaviour).

Calorimetric measurements provide information about the binding forces of the pollutant adsorbates. Whereas the low adsorption heat of the phenols on hydrophilic clay surfaces can hardly be measured, clearly exothermal enthalpies were determined for the adsorption of 4-nitrophenol on surfactant-bentonite complexes [23]. Accordingly, the hydrophobic interactions (hydrophobic bond) between the surfactant alkyl chains and the aromatic part of the pollutant molecules are of major importance for these adsorption processes.

On the whole, the displacement of adsorbed environmental chemicals by cationic compounds seems to be a process of general environmental relevance. Thus, for example, the pesticide atrazine adsorbed on layer silicates can be quantitatively displaced by the cationic plant growth inhibitor chlormequat [25], which may lead to a contamination of the ground water with atrazine. Furthermore, as a consequence of similar processes surfactants may also reach deeper layers of the soil and initiate further secondary reactions there.

Non-ionic Surfactants

Apart from the cationic surfactants, non-ionic surfactants also cause an increased hydrophobization of the layer silicate surface with increasing concentration, thus promoting, for example, the adsorption of the hydrophobic fungicide biphenyl (see Fig. 16) [26]. The increased biphenyl adsorption also measured at a very weakly hydrophobized bentonite (10 μmol non-ionic surfactant/g bentonite) indicates that these effects also become active even with very small (environmentally relevant) surfactant concentrations.

Anionic Surfactants

In the case of clay minerals pretreated with small amounts of anionic surfactants (e.g. sodium dodecylsulphate (SDS), c < CMC (critical micelle concentration)), for example, the adsorption

of biphenyl is not significantly influenced in comparison to pure layer silicates [26]. These findings may be explained, amongst other aspects, by the low adsorption potential for anionic surfactants of the negatively charged layer silicate surface (cf. Fig. 17, curve A). Quite different conditions exist in acid soils, in which the soil minerals may be positively charged. As expected, higher adsorbed quantities of anionic surfactants were found, for example, on aluminium oxide at pH 3 - 7 [27]. Even in the neutral pH range, increased anionic surfactant adsorption on soil minerals is possible if cationic or non-ionic surfactants are also present in the system. Adsorption from a mixture of anionic and non-ionic surfactant on kaolinite thus shifts the isotherms of both components towards smaller equilibrium concentrations [28], as illustrated by curve B in Fig. 17 for SDS in the presence of the non-ionic surfactant $C_{12}E_8$. At a mixing ratio of 1:1, a SDS concentration in the bulk phase lower by one power of ten is already sufficient to achieve the same SDS adsorption as without the addition of non-ionic surfactant. Since in real systems surfactant mixtures can almost always be expected, the processes shown may play a significant role in the adsorption of organic pollutants on inorganic soil constituents.

Pollutant Influences on Surfactant Adsorption

In the same way that surfactants may determine the mobility behaviour of environmental chemicals in the soil, surfactant transport may also be influenced by other accompanying substances. For example, surfactants adsorbed on layer silicates may be exchanged by ionic pesticides, as illustrated in Fig. 18 for a clay mineral precoated with DTAB [20]. The preferentially adsorbed organic dication paraquat (PQ) displaces the single charged DTAB (the substance quantities are given in equivalent quantities (eq) to clarify the comparison). For each equilibrium concentration, the associated adsorbed amounts of PQ and DTAB approximately correspond to the CEC. On the basis of these experimental findings, the following exchange reaction may be assumed:

$$(DTA^+)_2\text{-clay} + PQ^{2+} = PQ^{2+}\ \text{clay} + 2DTA^+.$$

Since in contrast to the cationic surfactants, the non-ionic surfactants are largely physisorbed on clay mineral surfaces, they can be relatively easily replaced by monocationic organic substances. If, for example, the monocationic pesticide cyperquat (CQ) is present in the soil electrolyte then apart from the essential cations (Ca^{2+}, Na^+) it also displaces the physisorbed non-ionic surfactant $C_{12}E_8$ [26]. In order to illustrate the associated structural changes at the layer silicate, Fig. 19 shows the basal spacing of an Na montmorillonite pretreated with $C_{12}E_8$ as a function of the adsorbed amount of CQ. The initial basal spacing of the clay-surfactant

complex (1.8 nm) caused by the intercalation of $C_{12}E_8$ decreases increasing amount of adsorbed CQ and at 1.5 nm finally reaches the basal spacing of pure CQ-montmorillonite.

On the whole, the following conclusions may be drawn as the provisional results of these model studies:

- Cationic surfactants mobilize essential elements and heavy metals in stoichiometric relations and are quantitatively adsorbed.
- Only cationic surfactants are capable of mobilizing Cd^{2+} whereas non-ionics do not display any effects and anionic surfactants cause an immobilization.
- The originally hydrophilic surface of the layer silicates is hydrophobized by the adsorption of cationic and non-ionic surfactants resulting in an expanded interlayer of the swellable clay minerals expanded.
- The adsorption of hydrophobic environmental chemicals is enhanced or accelerated at surfactant-clay mineral complexes. The extent of this enhancement depends on the degree to which the surface is hydrophobized.
- The inorganic soil horizon represents an effective sink for organic pollutants, whose effectiveness may increase considerably in the presence of small quantities of surfactant.
- Surfactants adsorbed on clays may be displaced by ionic pesticides, i.e. surfactant transport can also be influenced by other accompanying substances.

Conclusions

The results presented above as examples of the operation and accompanying research programme of the Environmental Specimen Bank represent an initial attempt to indicate perceptible developments in the chemical pollution of our environment on the basis of reliable data. Based on these results, it is already apparent that in concert with the "Ecological Environmental Monitoring" and the "Environmental Precautions Policy" of the Federal Government the Environmental Specimen Bank may be used as a most effective instrument to determine pollutant trends and to monitor the success of legislative measures. Even after the relatively short period of permanent operation, it has been possible to document the success of the introduction of unleaded fuels both in the environment and also in the human sector by the element characterization of representative samples. In future it will furthermore also be possible to monitor the impacts of modern environmental technologies on improving the quality of water and air by means of appropriate indicator systems. It is, moreover, of special significance that in particular those substances which cannot be determined now with the

necessary reliability or whose ecotoxicological or human toxicological effects are not yet known can be studied by retrospective monitoring with authentic samples from the past.

As a supplement to this work directed towards individual elements or substances, in future those investigations will have to be intensified which concern themselves with the synergistic or antagonistic effects of multicomponent systems. Major emphasis is placed on elucidating basic relations responsible for the mobilization or immobilization of pollutants under the influence of extraneous chemicals. Typical examples are the effects of surface-active substances on the bioaccumulation or bioavailability of environmental chemicals in soils or sediments.

Finally, on the basis of its application-related aims, the Environmental Specimen Bank offers the possibility of illustrating the significance and necessity of forward-looking environmental research to a broad section of the population. The Environmental Specimen Bank thus also makes a vital contribution towards providing an objective perspective for public discussions of environmental problems.

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Figure Captions:

Fig. 1: Accumulation of polychlorinated biphenyls (PCB) in various trophic stages of the marine environment

Fig. 2: Flow chart of the preparation of environmental specimens

Fig. 3: Organizational chart of the project "Environmental Specimen Bank of the Federal Republic of Germany"

Fig. 4: Geographical map of the representative sampling areas for the Environmental Specimen Bank

Fig. 5: Various selected sample types from different sectors of the environment

Fig. 6: Decline in lead pollution from wet deposition in rural areas (site: Jülich) and in spruce shoots from a "background area" (site: Berchtesgaden National Park)

Fig. 7: Displacement of Na^{+} and Cd^{2+} ions from a layer silicate by cationic surfactant [11]; (DTAB = dodecyl trimethyl ammonium bromide)

Fig. 8: Distribution of mercury concentrations in Elbe sediments from 1991 and 1992 along the Elbe at sampling sites of the International Commission on Protection of the Elbe; Schmilka - border Czech Republic/Germany; Barby - Saale estuary; Cumlosen - former boundary between the two German states

Fig. 9: Time curve of the lead and cadmium concentration in surface sediments of the Rhine (site: Emmerich); for comparison, values in Elbe sediments from 1991 at the Cumlosen site

Fig. 10: Distribution of the thallium concentration in bream muscle from Lake Constance and the Bornhöved Lake district

Fig. 11: Accumulation of mercury in various trophic stages of the marine environment

Fig. 12: Accumulation of various elements in (a) edible mussels and (b) bladder wrack from the North Sea (N) and the Baltic Sea (B)

Fig. 13: Decline in mercury pollution in the estuary regions of the Elbe (Island of Trischen) and Weser (Island of Mellum) represented by the pollution values of herring gull eggs; FG = fresh weight

Fig. 14: Cd^{2+} mobilization from degraded loess soil by various classes of surfactant:
didodecyl dimethyl ammonium bromide;
sodium dodecyl sulphate;
alkylphenyl polyethylene glycol ether (Triton-X-100) with 9.5 EO

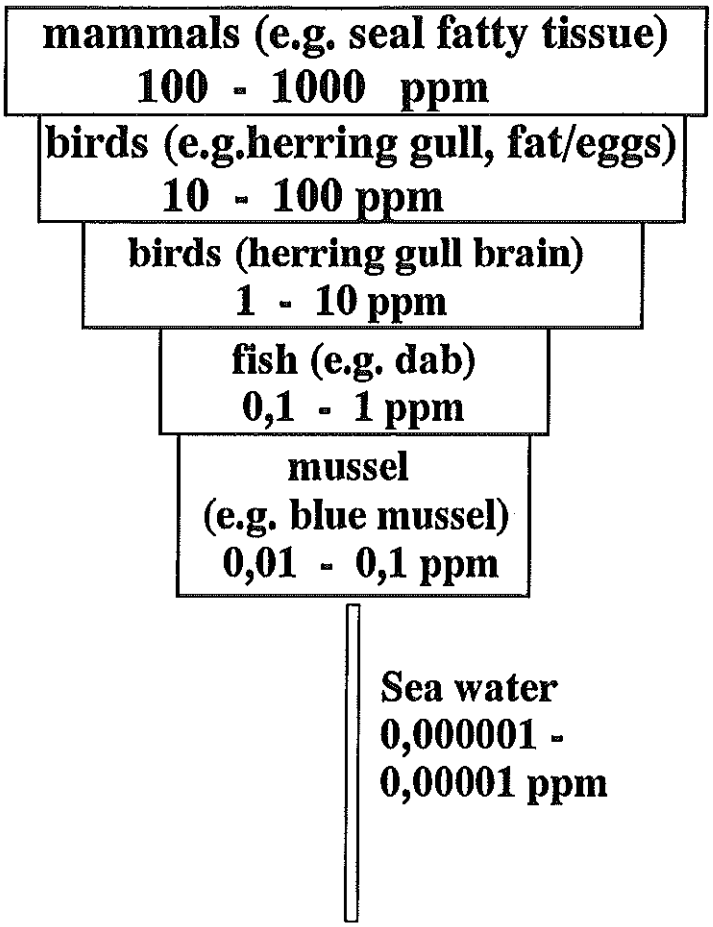
Fig. 15: Adsorption isotherms of 2-naphthol on cetyltrimethyl ammonium (CTA^+)-illite with increasing surfactant coverage (related to the CEC)

Fig. 16: Adsorption isotherms of biphenyl on bentonite in the presence of the non-ionic surfactant dodecyl octaethylene glycol ether ($C_{12}E_8$): (x - x without surfactant; with 0.013 mmol/g $C_{12}E_8$; with 0.3 mmol/g $C_{12}E_8$) [26]

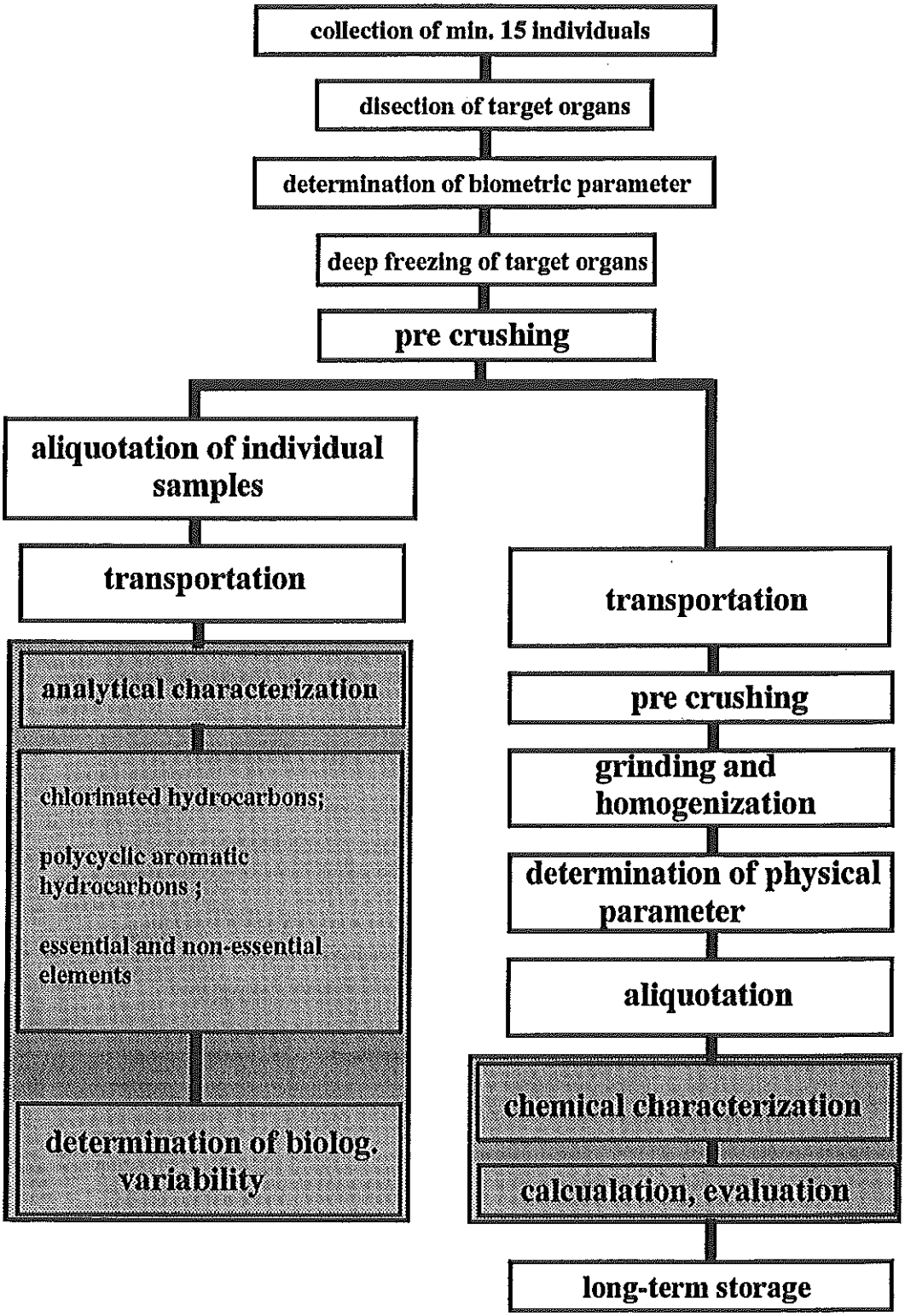
Fig. 17: Adsorption isotherms of sodium dodecylsulphate on kaolinite. (A): without non-ionic surfactant; (B): with the addition of dodecyl octaethylene glycol ether in the ratio 1:1 [28]

Fig. 18: Adsorption of paraquat on Ca-bentonite pretreated with cationic surfactant: adsorption isotherm of paraquat, displacement of dodecyl trimethyl ammonium bromide (DTAB). (DTAB pretreated 0.73 meq/g) [20]

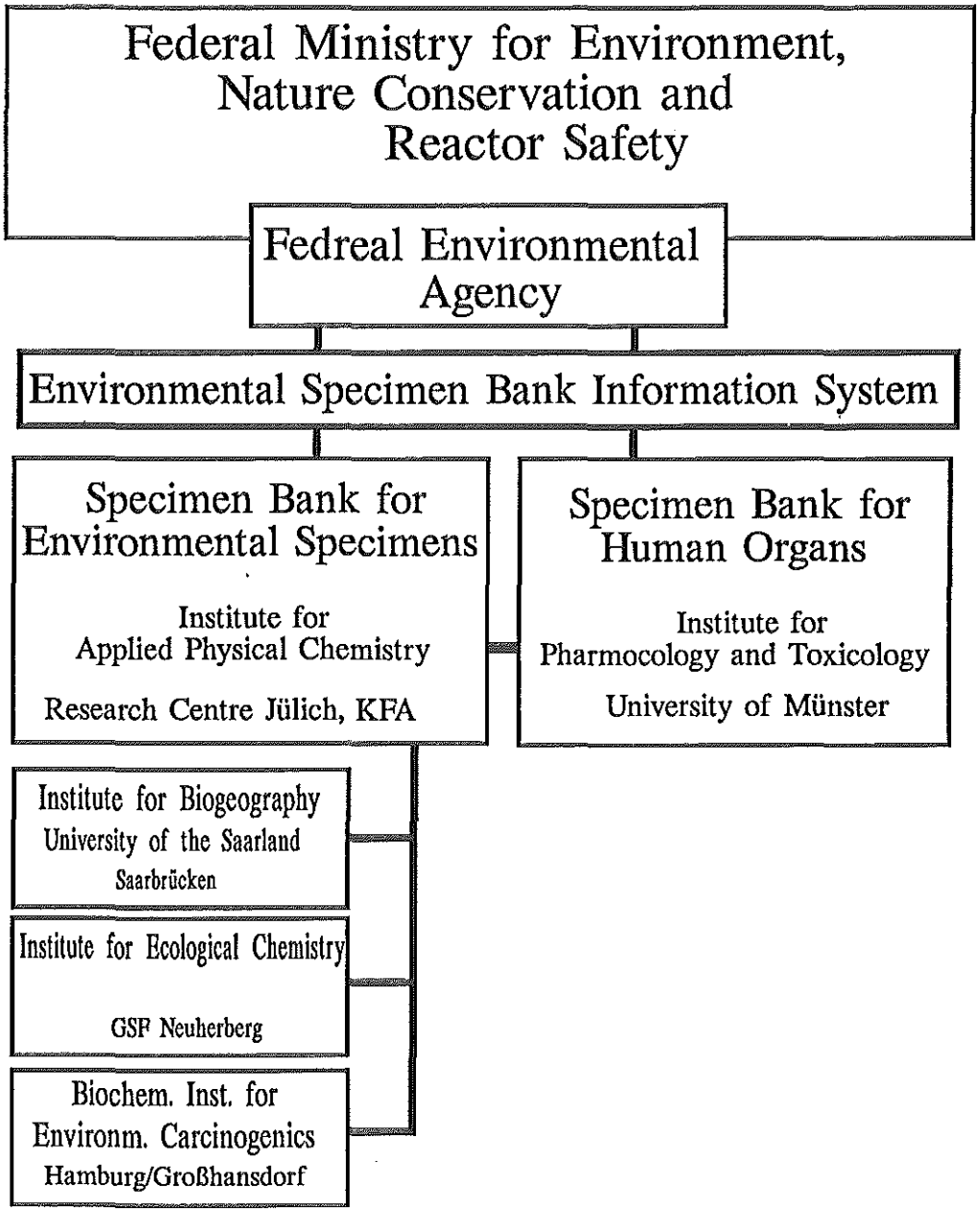
Fig. 19: Change in the basal spacing of Na montmorillonite with the addition of cyperquat (1), dodecyl octoethylene glycol ether (2) as well as cyperquat to montmorillonite precoated with $C_{12}E_8$ (3) [26]

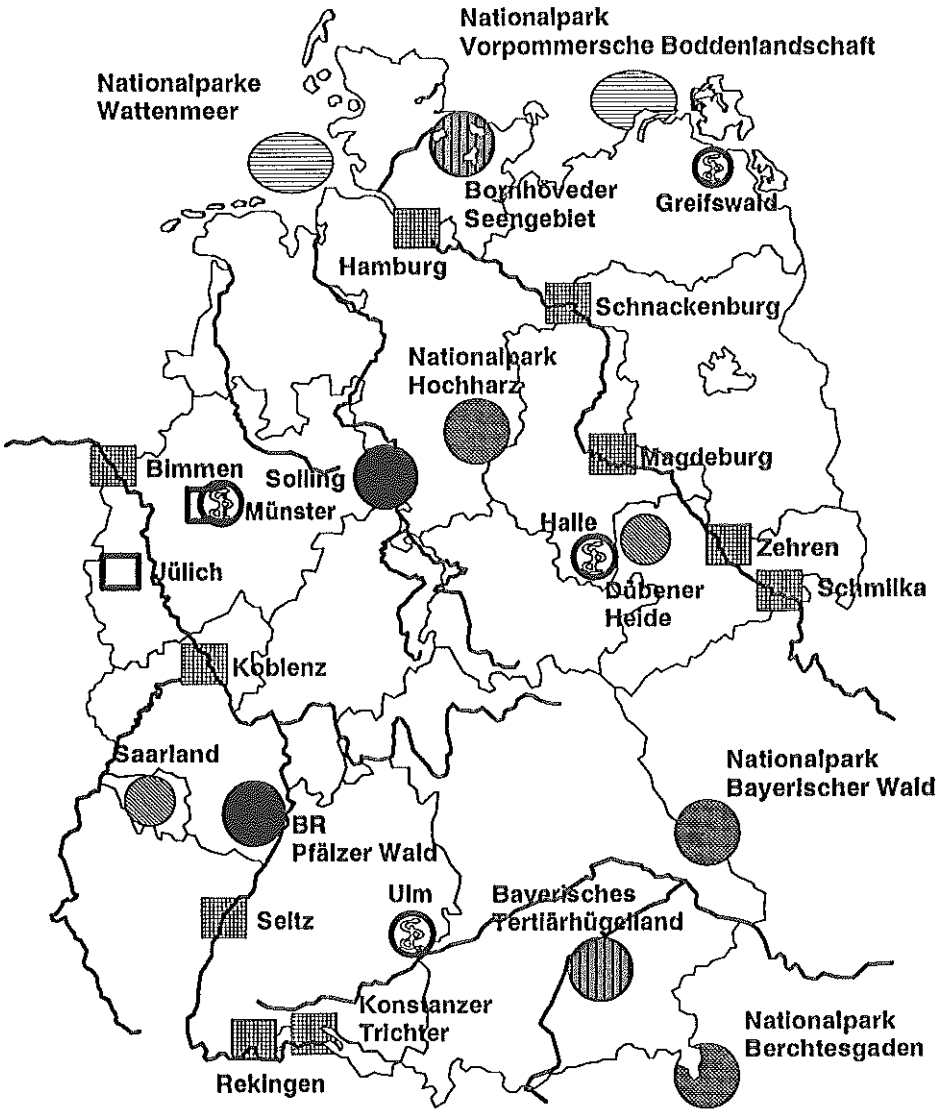


PCB food limit value for fish in the U.S. :
< 2ppm


collection of min. 15 individuals
disection of target organs
determination of biometric parameter
deep freezing of target organs
pre crushing
aliquotation of individual samples
transportation
analytical characterization
chlorinated hydrocarbons;
polycyclic aromatic hydrocarbons ;
essential and non-essential elements
determination of biolog. variability
transportation
pre crushing
grinding and homogenization
determination of physical parameter
aliquotation
chemical characterization
calcualation, evaluation
long-term storage

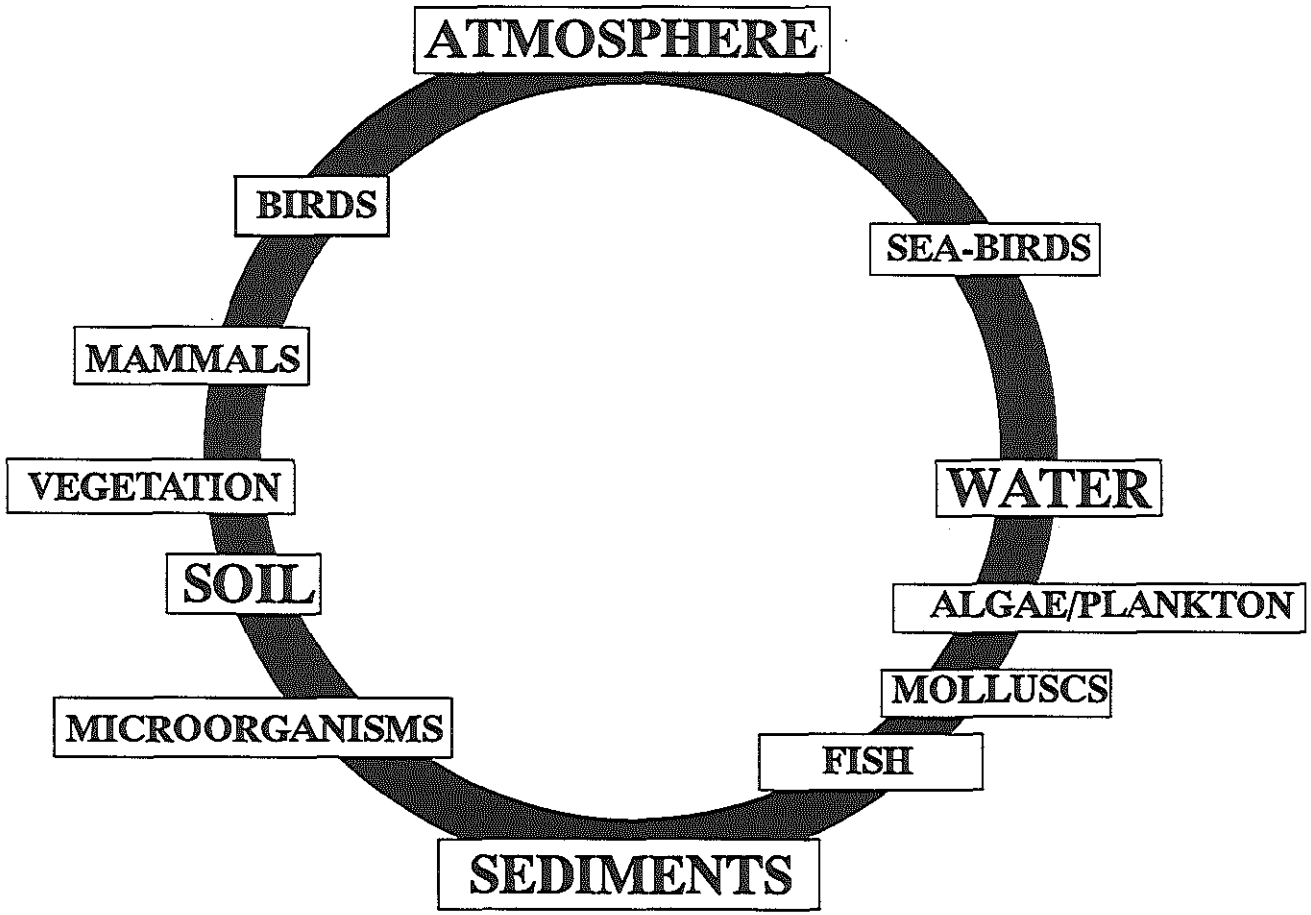
ENVIRONMENTAL SPECIMEN BANK of the FEDERAL GERMAN GOVERNMENT

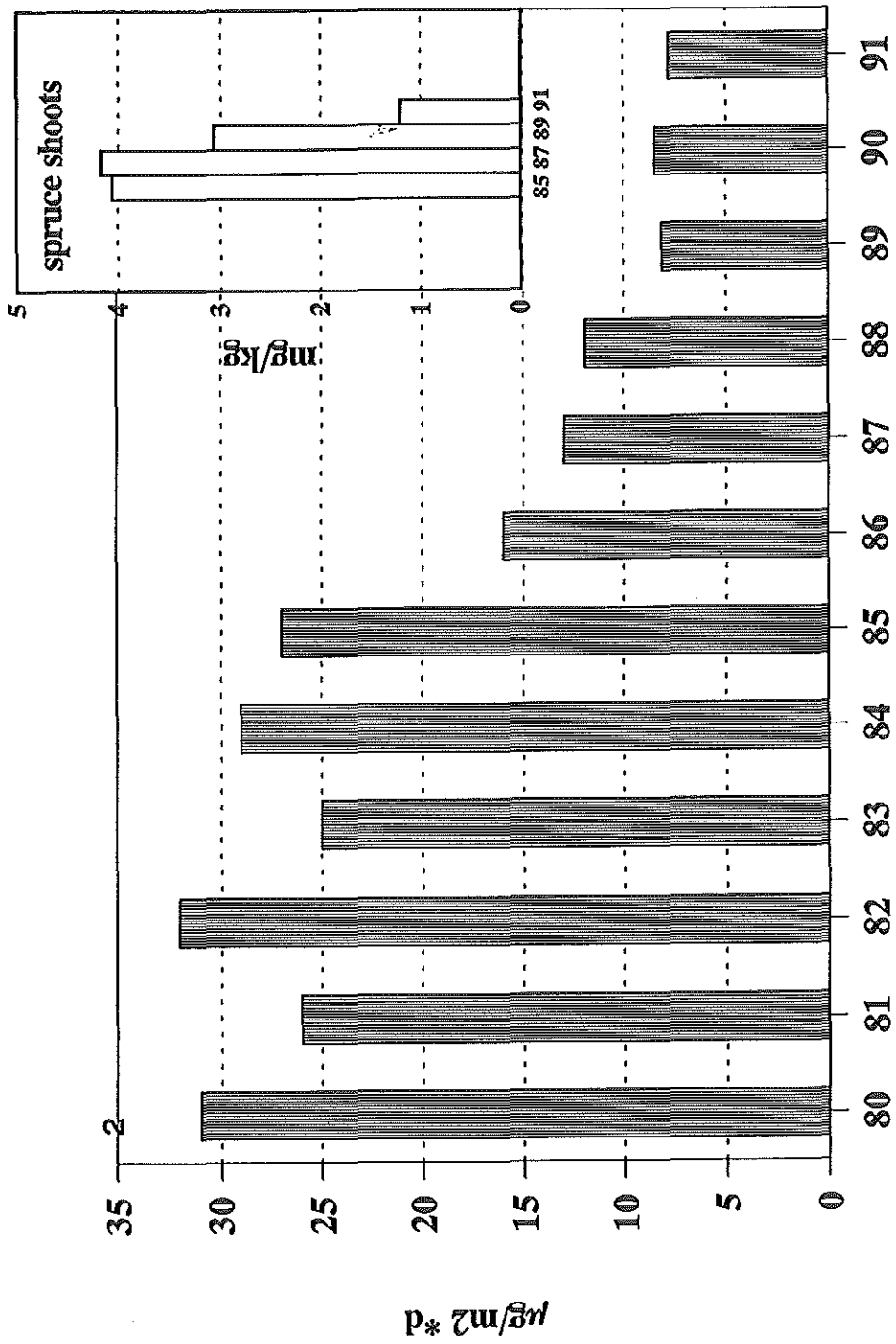


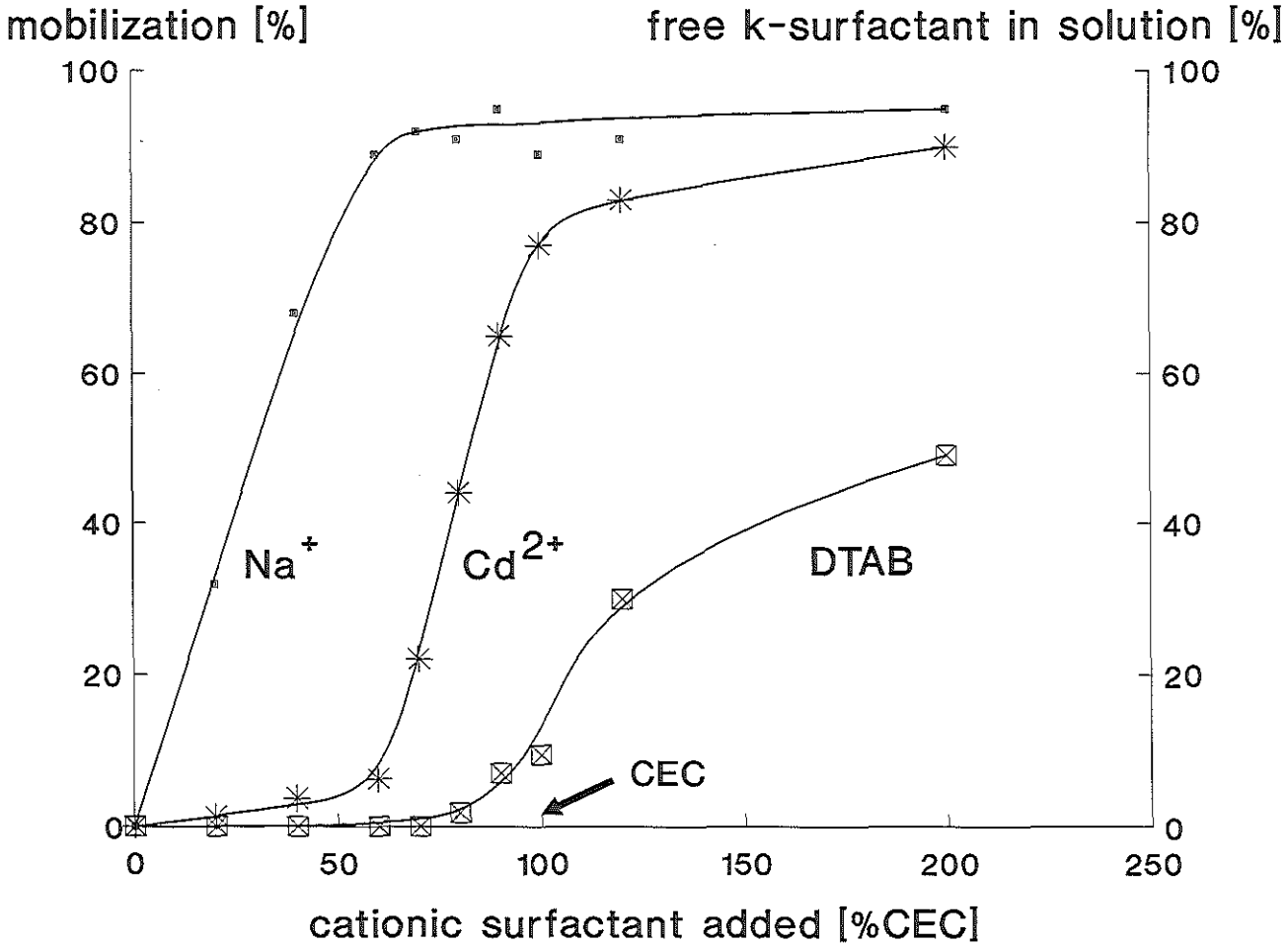


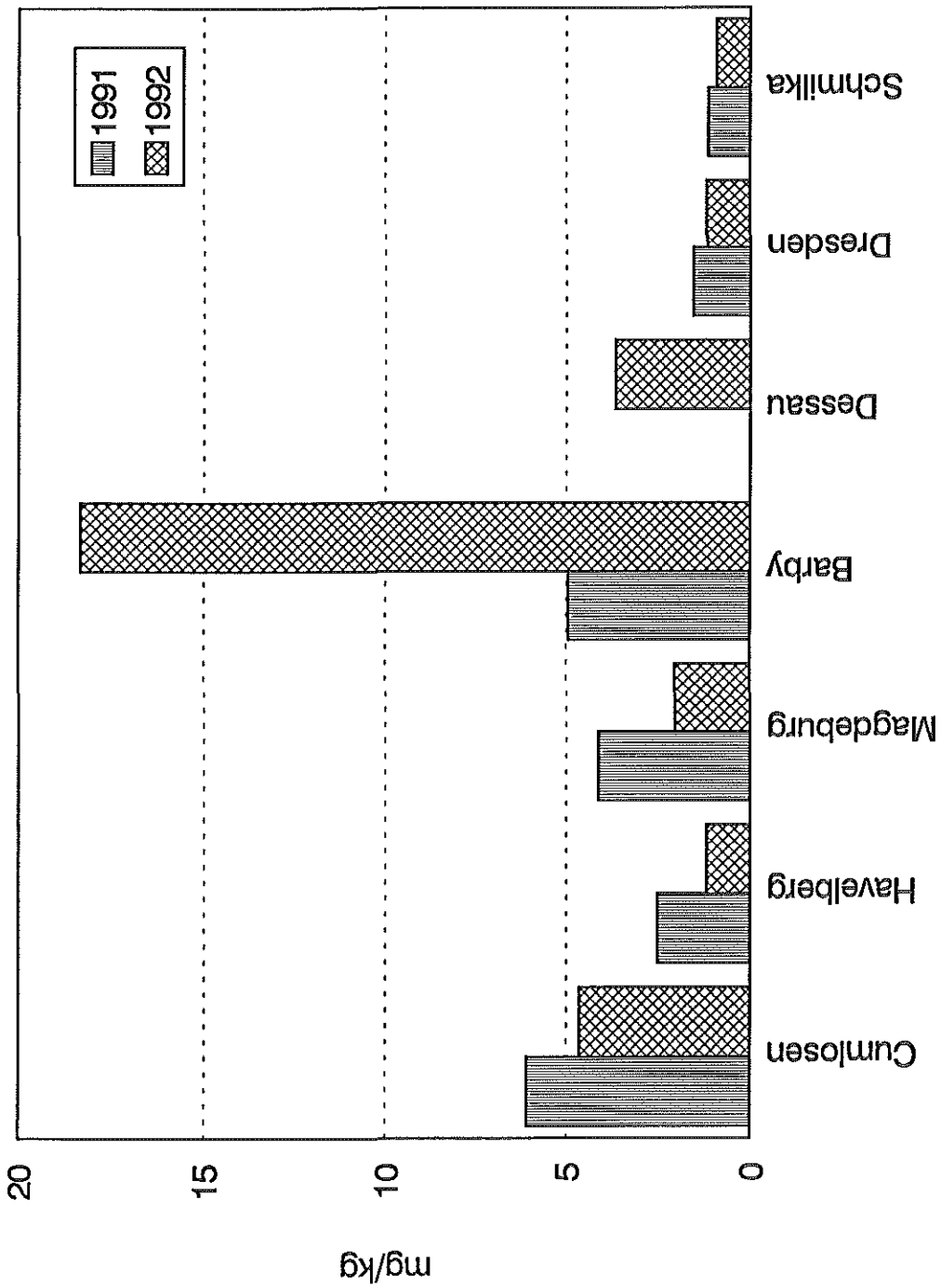
Types of Ecosystem :

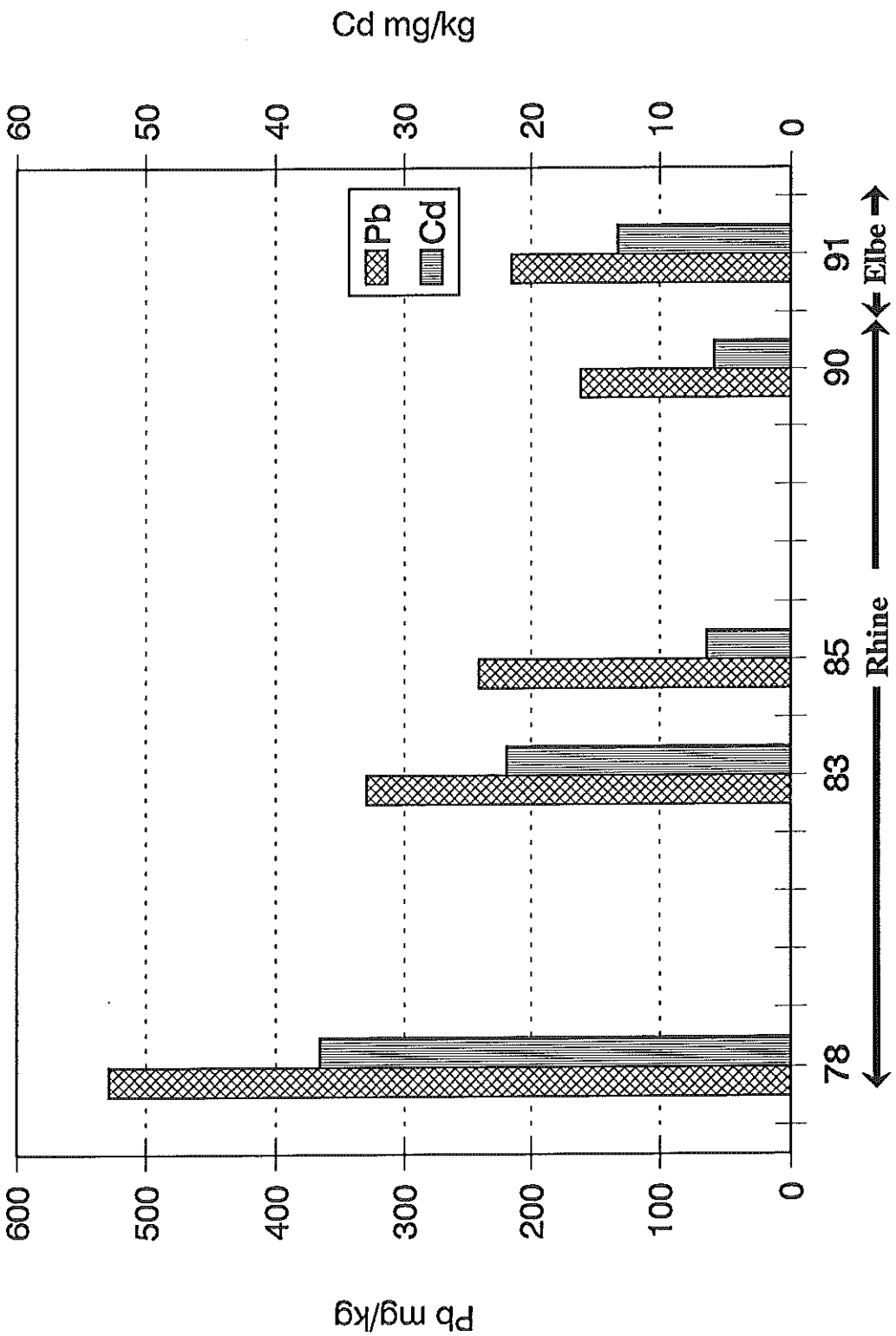
agricultural
semi-natural
forestreal
urban-industrialized
limnic
marine
human organ specimens
ESB - facilities

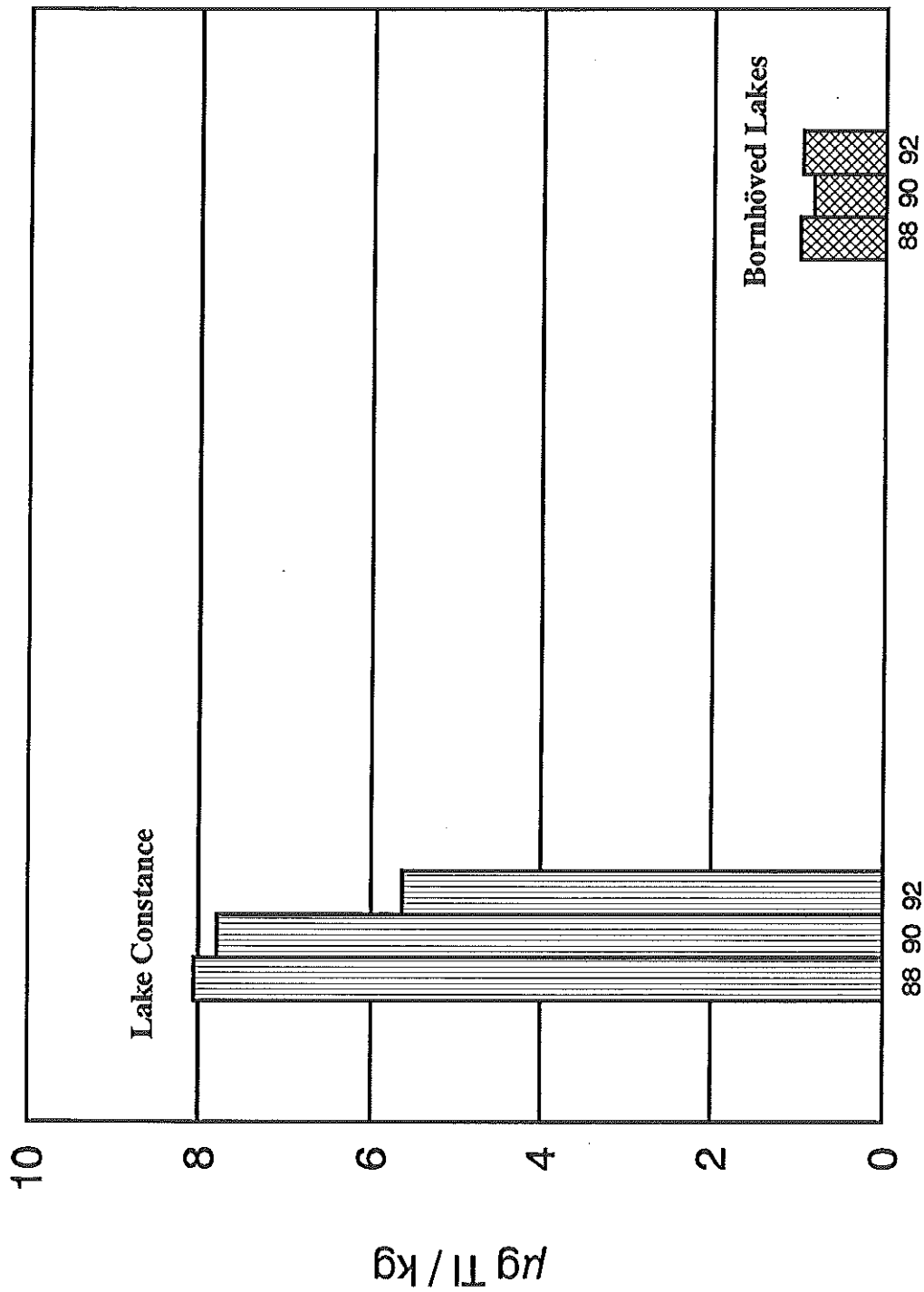

ATMOSPHERE
BIRDS
SEA-BIRDS
MAMMALS
VEGETATION
WATER
SOIL
ALGAE/PLANKTON
MOLLUSCS
MICROORGANISMS
FISH
SEDIMENTS

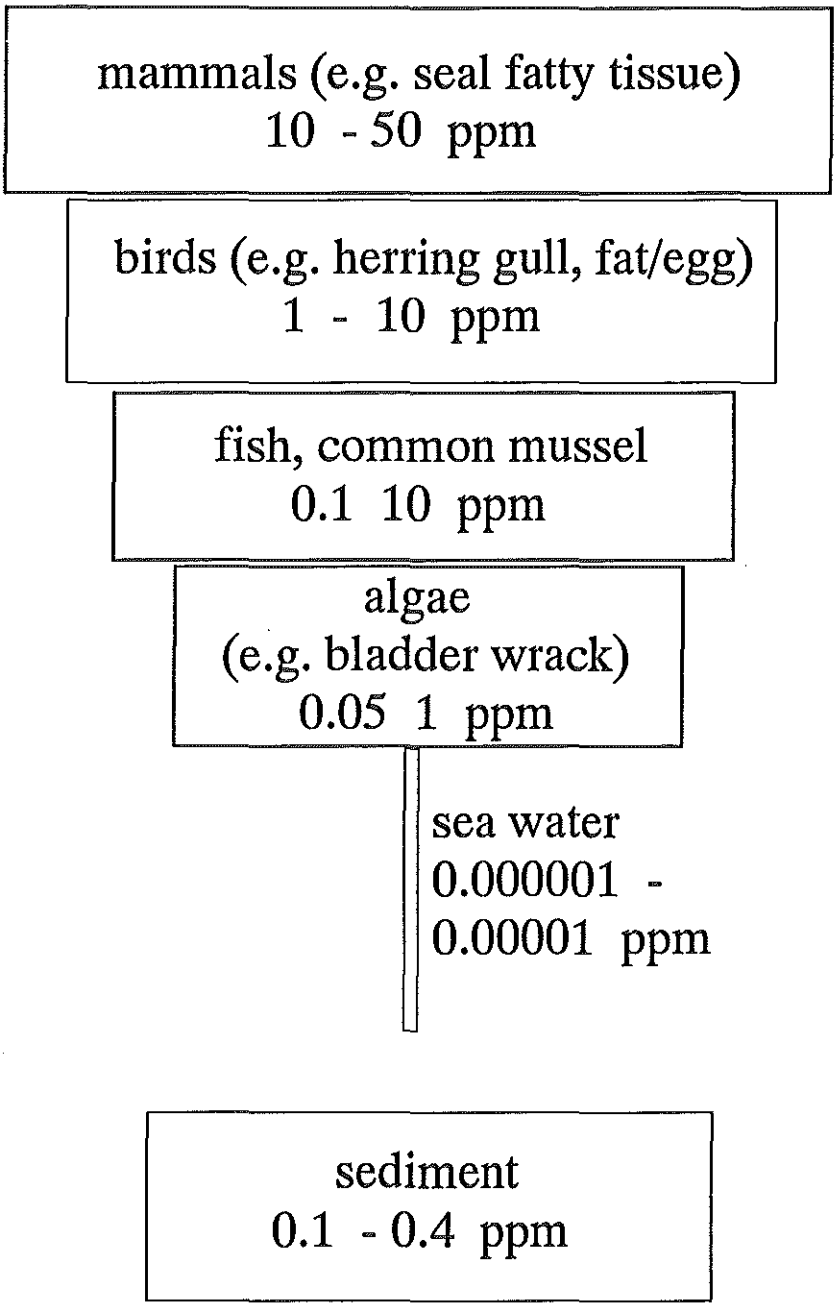

spruce shoots
mg/kg
85 87 89 91
µg/m2 *d
80
81
82
83
84
85
86
87
88
89
90
91


mobilization [%]
free k-surfactant in solution [%]
100
80
60
40
20
0
0
50
100
150
200
250
Na+
Cd2+
DTAB
CEC
cationic surfactant added [%CEC]

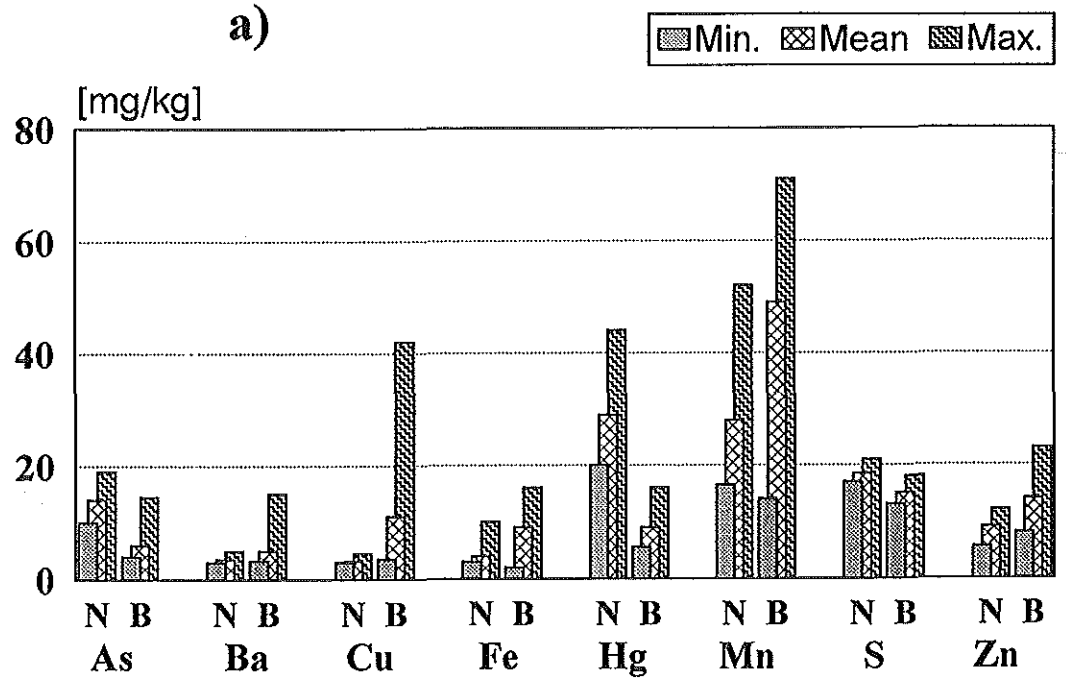

1991
1992
Schmilka
Dresden
Dessau
Barby
Magdeburg
Havelberg
Cumlosen
0
5
10
15
20
mg/kg


Cd mg/kg
60
50
40
30
20
10
0
Pb
Cd
91
90
85
83
78
Elbe
Rhine
600
500
400
300
200
100
0
Pb mg/kg


Lake Constance
Bornhöved Lakes
88 90 92
88 90 92
0
2
4
6
8
10
µg Tl / kg

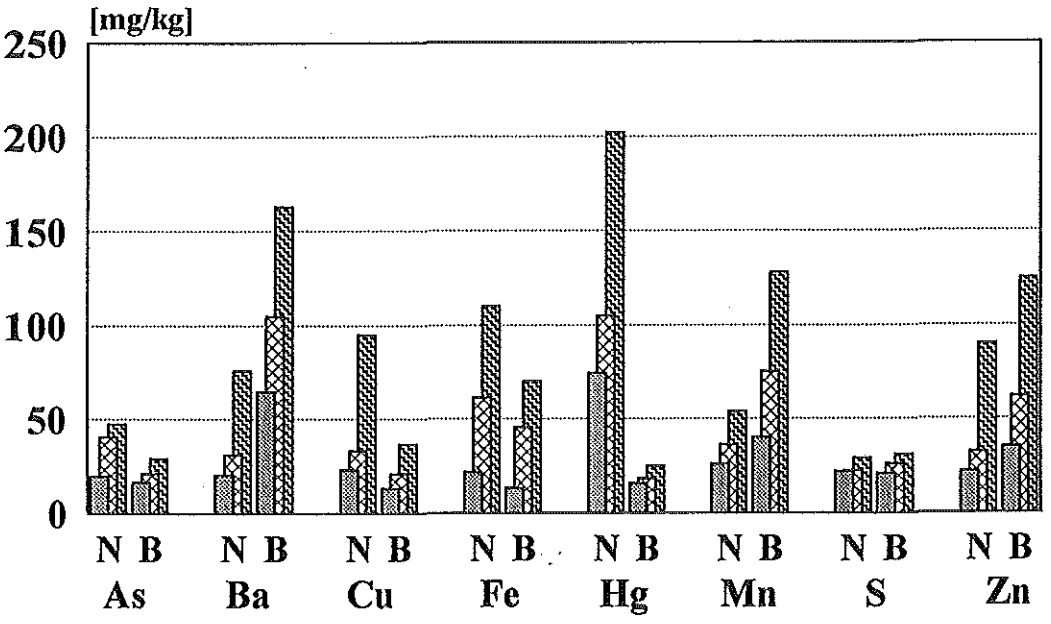

mammals (e.g. seal fatty tissue)
10 - 50 ppm
birds (e.g. herring gull, fat/egg)
1 - 10 ppm
fish, common mussel
0.1 10 ppm
algae
(e.g. bladder wrack)
0.05 1 ppm
sea water
0.000001 -
0.00001 ppm
sediment
0.1 - 0.4 ppm

a)

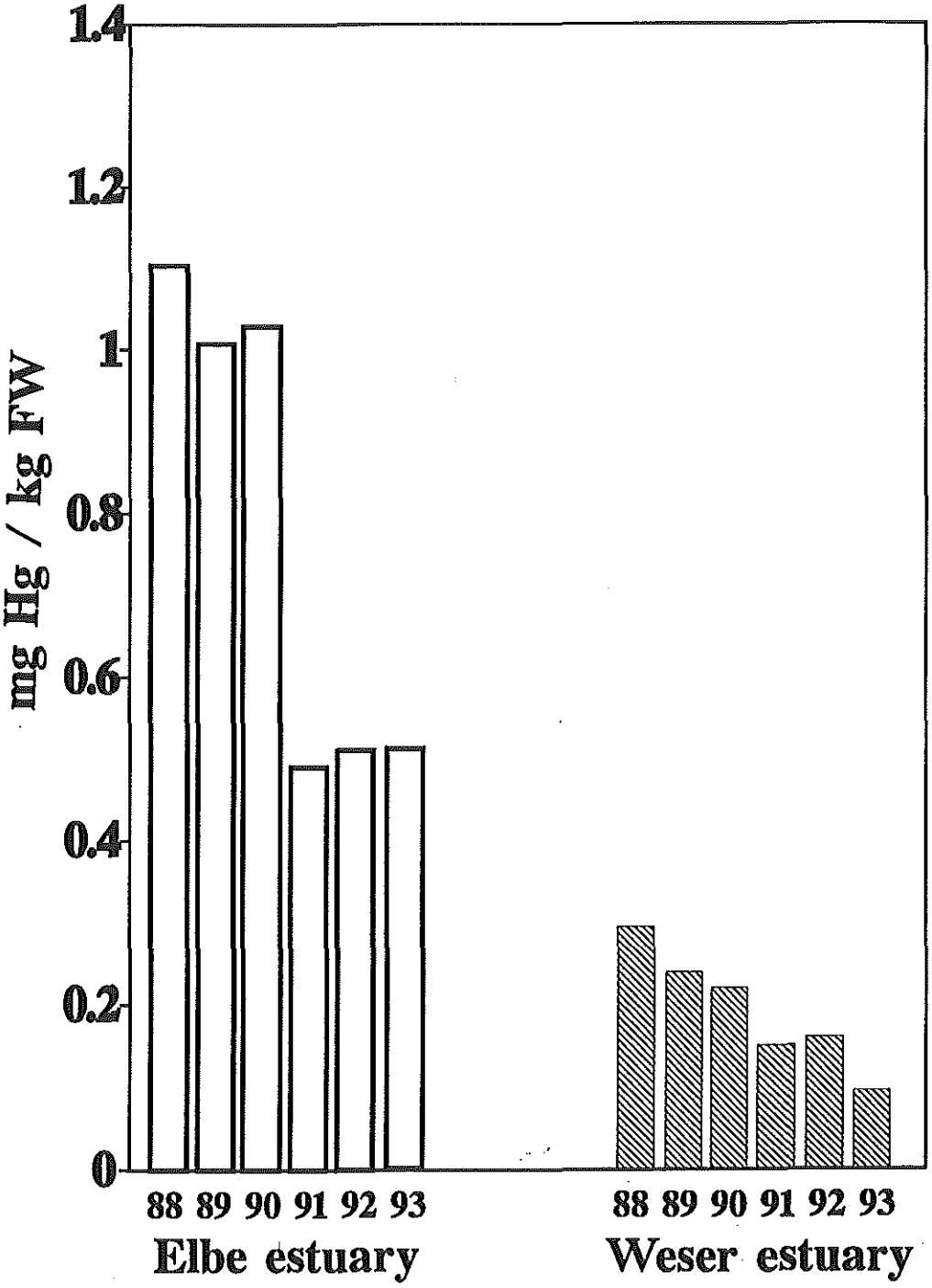


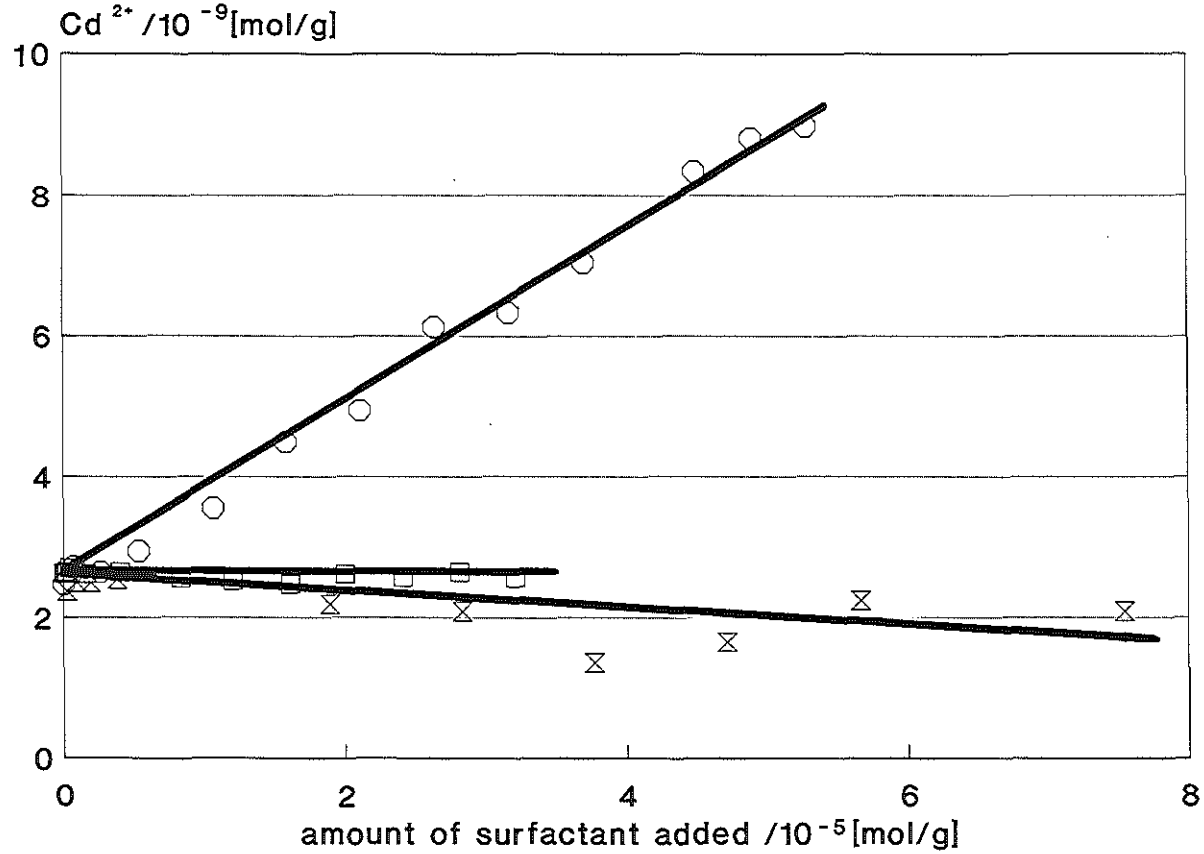
Hg [µg/kg], Fe [mg/kg x 0.01], Zn [mg/kg x 0.1]

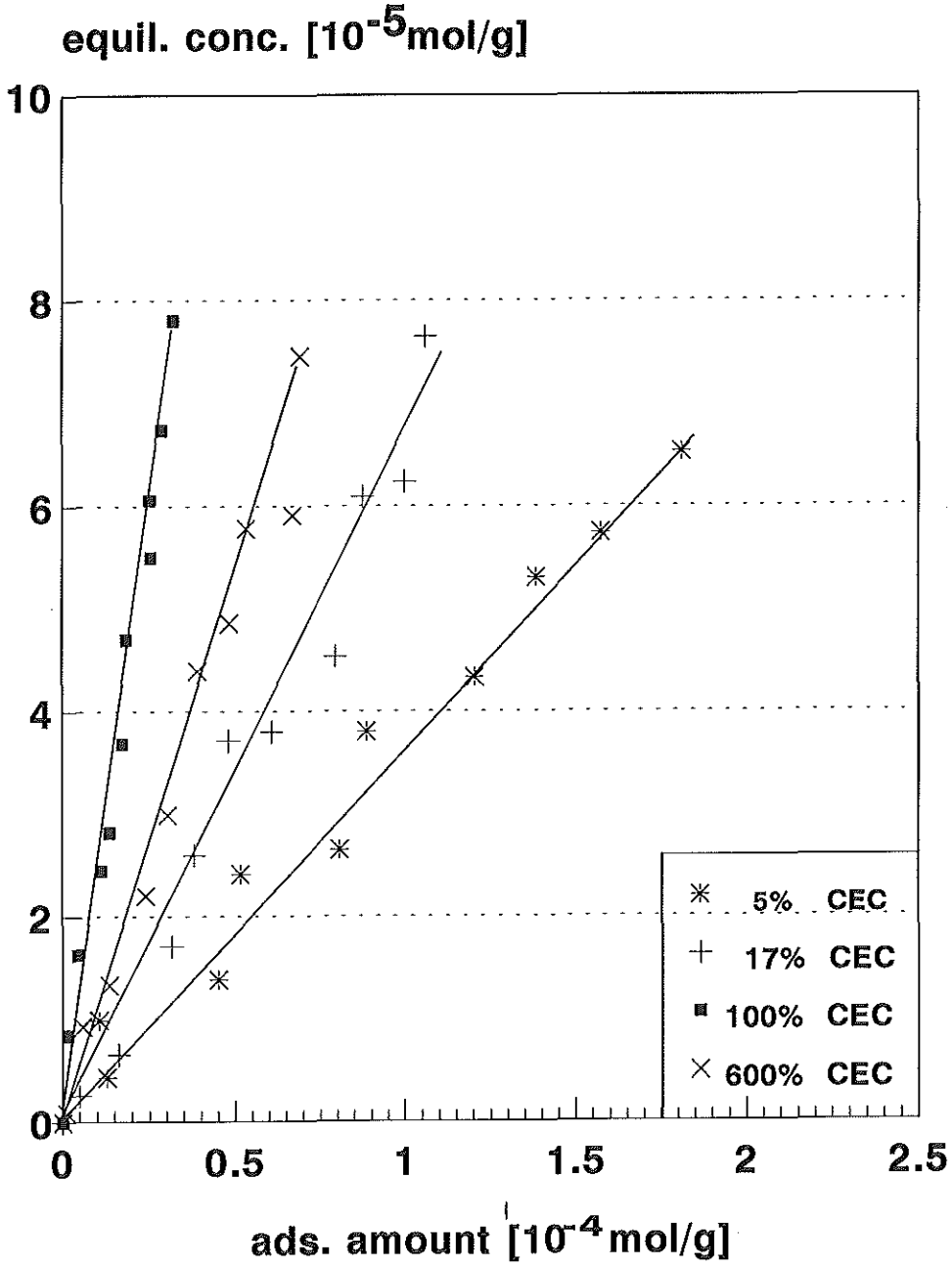
b)

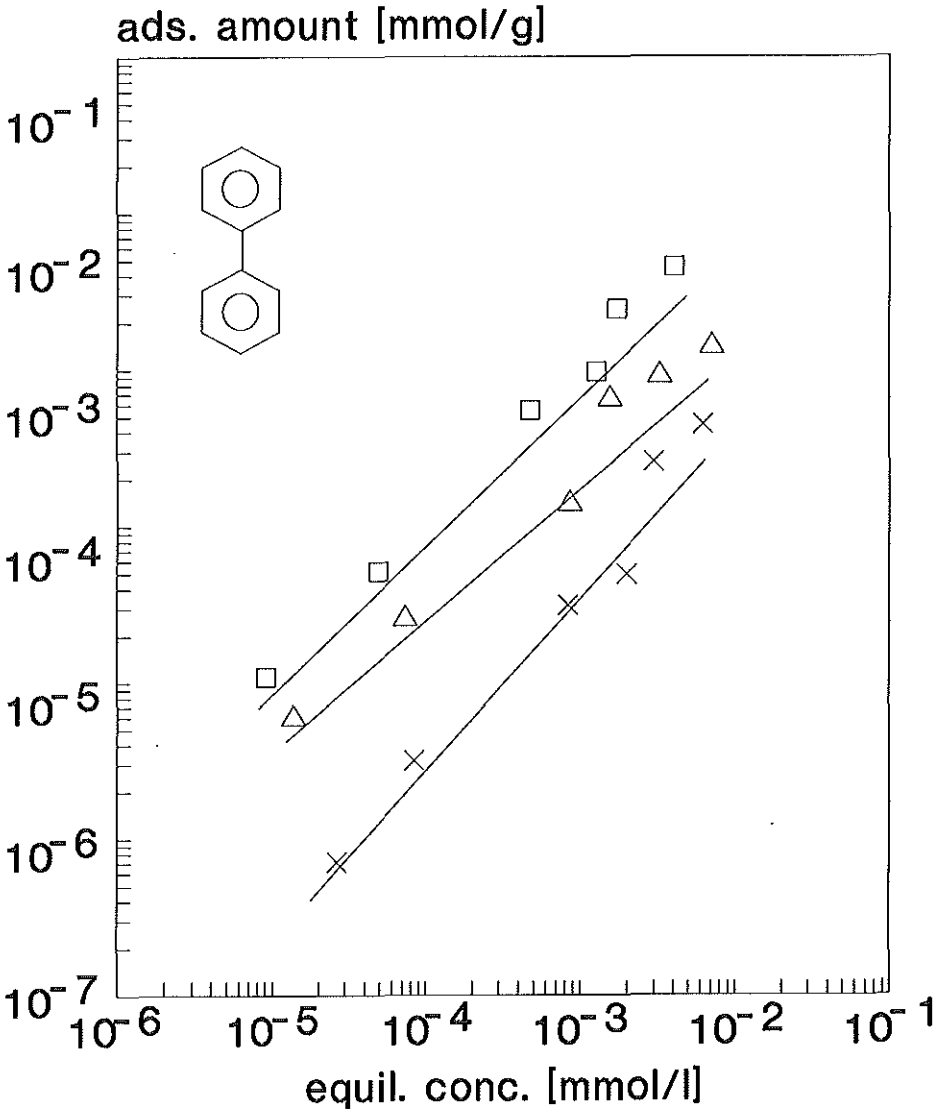


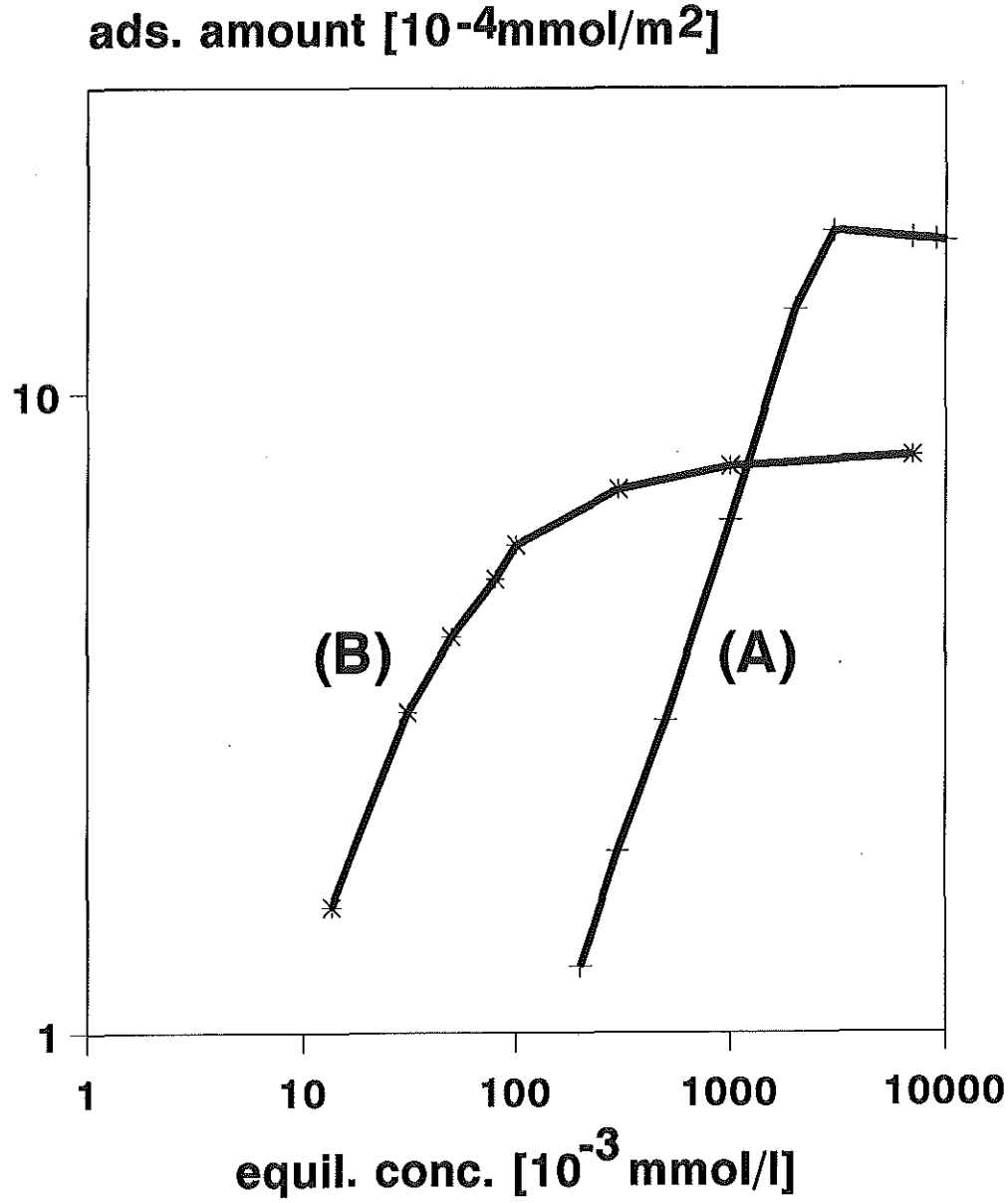
Hg [µg/kg x 10], Cu [mg/kg x 10], Fe and Mn [mg/kg x 0.1]


1.4
1.2
1
0.8
0.6
0.4
0.2
0
mg Hg / kg FW
88 89 90 91 92 93
Elbe estuary
88 89 90 91 92 93
Weser estuary


Cd 2+ /10 -9[mol/g]
10
8
6
4
2
0
0
2
4
6
8
amount of surfactant added /10 -5[mol/g]


equil. conc. [10-5mol/g]
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
ads. amount [10-4mol/g]
5% CEC
17% CEC
100% CEC
600% CEC


ads. amount [mmol/g]
10-1
10-2
10-3
10-4
10-5
10-6
10-7
10-6
10-5
10-4
10-3
10-2
10-1
equil. conc. [mmol/l]


ads. amount [10-4mmol/m2]
10
1
(B)
(A)
1
10
100
1000
10000
equil. conc. [10-3 mmol/l]

Inorganic Analysis within the German Environmental Specimen Bank

H. Emons

Institute of Applied Physical Chemistry, Research Center of Jülich, D-52425 Jülich, Germany

Introduction

The chemical characterization of environmental samples collected within the frame of the German Environmental Specimen Bank (ESB) Program is a challenging task for analytical chemistry and physical chemistry as well. There are high demands on accuracy and precision of analytical data describing the state of our environment and its changes because they are the basis of legislative actions to protect mankind and influence significantly our economic and social conditions. Environmental changes should be reliably recognized on the trace level for the purpose of an early warning system. Moreover, a large number of well-selected samples has to be characterized within a reasonable time.

Therefore, established analytical procedures have to be specified according to the different and difficult nature of environmental matrices as well as to the low concentration ranges in which many of chemical species with significant environmental importance are present. Modern state-of-the-art methods are applied for the characterization of environmental specimen bank samples [1] according to standardized procedures of the ESB. In addition, the analytical armoury has to be improved and extended permanently to increase the amount of information gained from the ESB samples. In the following the methods for inorganic analysis of ESB samples and some selected results from recent years will be described.

Analytical Methods

The strategy for inorganic analysis of ESB samples is shown in Fig. 1. At first the cold vapor atomic absorption spectrometry (CV-AAS) is used in a modified version for the determination of mercury and methyl mercury in fresh samples. Afterwards, the other elements are determined after a standardized drying process.

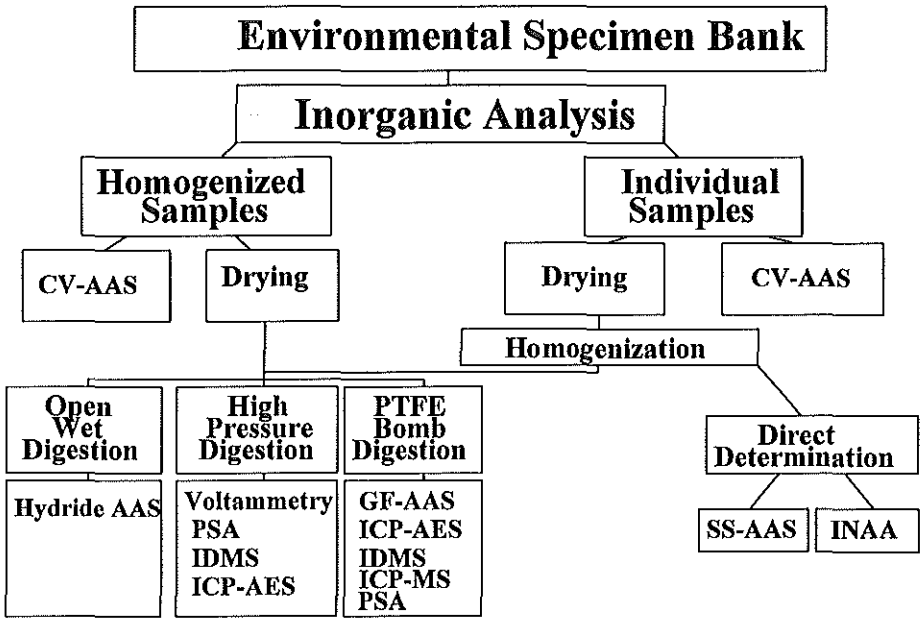


Fig. 1: Flow diagram for inorganic analysis of ESB samples

Solid-state atomic absorption spectrometry (SS-AAS) is applied for the characterization of the homogenity within a sample container and between sample containers. Instrumental neutron activation analysis (INAA) allows to study contamination problems during different digestion procedures as well as the direct determination of elements not accessible by other techniques. At present both techniques are only used for selected samples because of their dynamic ranges and the time and manpower necessary for performing the analysis.

All the other approaches are typical so-called "wet analysis" methods. As a result solid sample material has to be digested before the determination steps. Various digestion techniques were developed and evaluated during the pilot phase of the Environmental Specimen Bank. It had been shown that analytical sample preparation is the most critical step for obtaining accurate and precise analytical data. As a result those procedures were optimized in dependence on the matrix to be analyzed and the detection technique to be used [2].

The analytical methods were selected with the emphasis on trace analysis capability and applicability for very complex biological matrices. They can be devided into four groups, namely various versions of atomic spectrometry, mass spectrometry, electrochemical, and radiochemical methods.

Atomic Spectrometry

Single element techniques are used such as electrothermal graphite furnace AAS (GF-AAS), CV-AAS, and hydride AAS as well as multielement techniques such as inductive coupled plasma atomic emission spectrometry (ICP-AES). The analytes which are determined by these methods are summarized in Fig. 2.

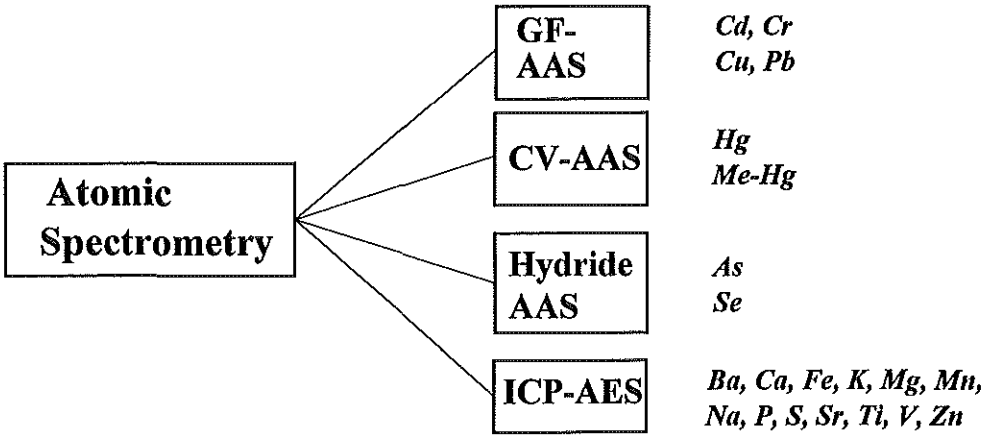


Fig. 2: Analytes determined by different methods of atomic spectrometry

It is important to note, that the detection limits related to the dry weight of bioindicators are different for the atomic spectrometric methods. The ICP-AES technique is only suitable for concentration ranges down to the low ppm level, whereas GF-AAS can be applied down to approximately 20-50 ppb without an accumulation step. Hydride AAS detects As or Se also on the level of 0.5 ppb. The modified version of CV-AAS developed at the Institute of Applied Physical Chemistry [3] is applicable even for the ulta-trace analysis of Hg down to about 10 ppt. A special advantage of the latter technique consists in its capability to determine separately the total mercury content and the amount of methyl mercury, respectively, in biological and environmental samples.

Mass Spectrometry

An overview about the elements determined by other methods is shown in Fig. 3.

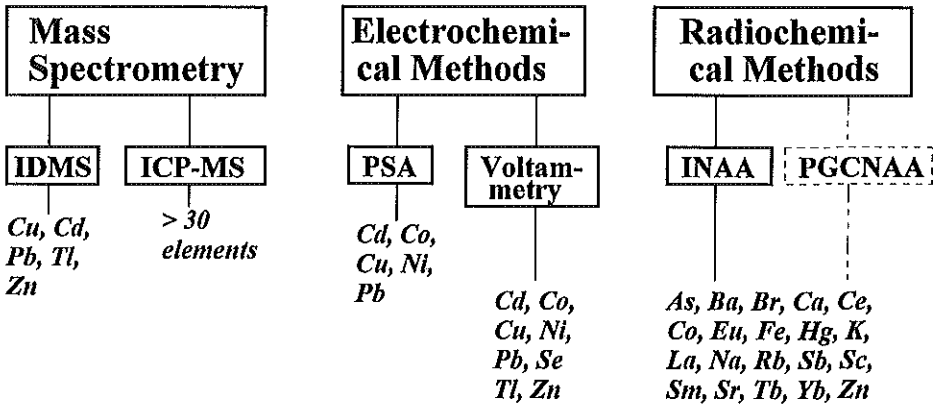


Fig. 3: Analytes determined by other analytical methods in ESB samples

Isotope dilution mass spectrometry (IDMS) with thermal ionization has been proved to be a powerful technique for trace analysis, particularly in the case of thallium. Recently, procedures were developed for the determination of Tl in environmental samples down to the low ppt level [4]. Such detection limits are necessary for the monitoring of Tl in fishes or sediments and can be achieved by a combination of electrolytic accumulation and IDMS.

In the last years a new hyphenated analytical method called ICP-MS has been developed [5] and its instrumentation is available now commercially. In addition to the well-established application of ICP-MS to water analysis the method is presently introduced into the characterization of sediments and biological material. Because of its capability of multielement detection on the trace level the method can improve the efficiency of environmental analysis.

Electrochemical Methods

Modern electroanalytical techniques are well-suited for the trace analysis of an increasing number of inorganic species because of the possibility to combine an *in situ* accumulation step with sensitive detection based on Faradaic processes [6]. Two groups of the so-called stripping methods are presently used within the ESB.

Voltammetric methods based on the measurement of current-potential curves in electrochemical cells are applied after an accumulation of the analyte of interest by either potential-controlled reduction (anodic stripping voltammetry) or adsorption of appropriate chelate complexes at the electrode surface (adsorptive or cathodic stripping voltammetry). From the broad armoury of potential-time excitation signals the techniques of differential pulse voltammetry and square wave voltammetry were selected for the detection step. As a result concentrations down to the sub-ppb level can be determined.

The other approach consists in the application of potentiometric stripping analysis (PSA). Herein, the same accumulation procedures as in voltammetry are used but after this first step the potentiostat is switched off and the accumulated analyte is either oxidized by chemical species in solution such as oxygen and Hg^{2+}, respectively, or a galvanostatic reduction of adsorbed complexes occurs. The measuring curve is always a potential-time signal based on the Nernst equation which can be differentiated for the purpose of more sensitive data evaluation.

Radiochemical Methods

As mentioned above INAA is primarily used for the characterization of selected solid samples. It offers also analytical information about many rare earth elements which may be important for future environmental discussions. Moreover, INAA is applied as reference method for internal quality control activities.

A very new development within the ESB consists in the introduction of another radiochemical technique, the prompt gamma cold neutron activation analysis (PGCNAA) [7]. This method is particularly useful for the quantitative analysis of elements with low atomic weight such as B, C, N, S or P and a number of elements with exceptionally large cross sections for the absorption of neutrons such as Cd and Gd.

Selected Results

In the following recent results will be presented which were obtained by the application of analytical methods discussed above.

An important aspect of the ESB consists in the long-term monitoring of heavy metals in biological samples. In Fig. 4 the content of As in herring gull eggs is compared for two sampling sites in the North Sea (Islands of Trischen and Mellum) with one in the Baltic Sea (Heuwiese).

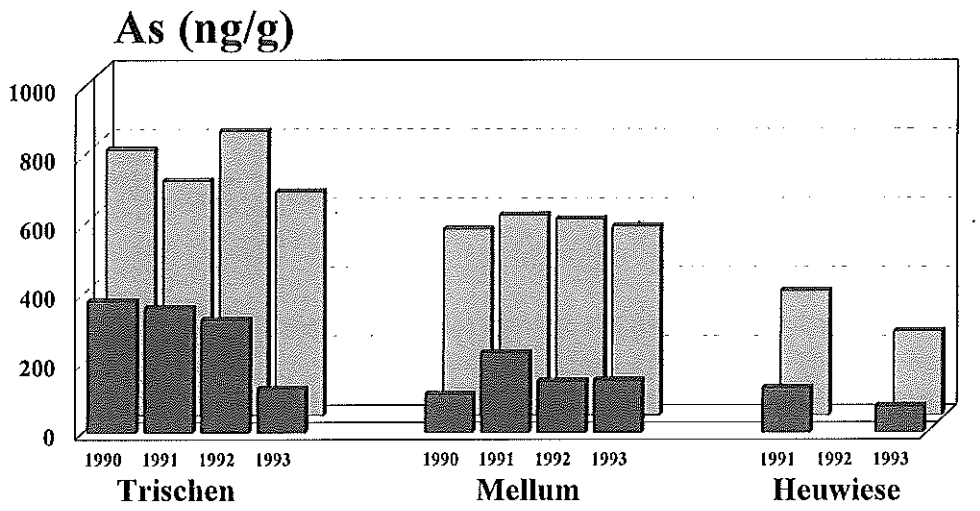


Fig. 4: Minimum and maximum content of As in single herring gull eggs at different sampling sites between 1990-1993

It is obvious that birds living in the estuary of the River Elbe (Trischen) show higher uptakes of As than species living in the estuary of the River Weser (Mellum) or in the Baltic Sea (Heuwiese).

Another objective of the ESB is the characterization of local pollution patterns in dependence on the sampling site within an ecosystem at a certain moment. The Fig. 5 illustrates this approach for the content of mercury and methyl mercury in bream kidneys from the River Elbe.

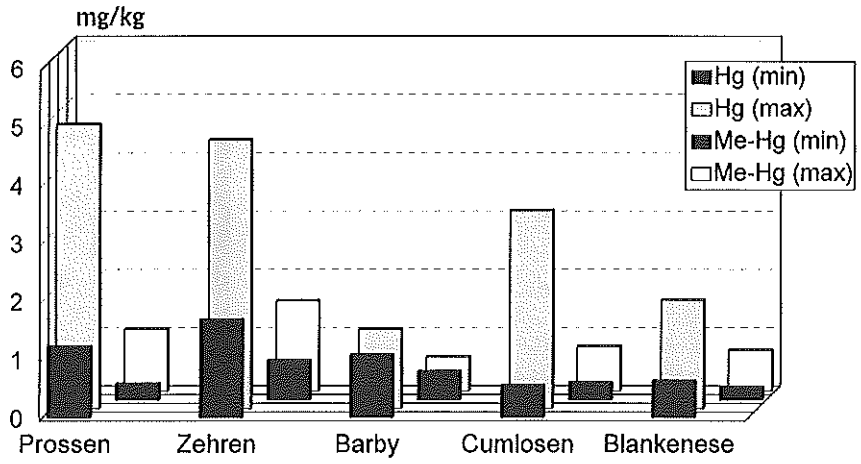


Fig. 5: Mercury and methyl mercury in bream kidneys from the River Elbe sampled in 1993

The sampling site Prossen is located near the German-Czechian border and the other sites are arranged downstream up to Hamburg (Blankenese). Significant maxima of the Hg uptake by these bioindicators were found whereas the concentration of the dangerous organic mercury species, the methyl mercury, varies only slightly.

The analytical results can also be used to evaluate different bioindicators with respect to their ability to monitor sensitively heavy metal contaminations. In Fig. 6 the Tl content of bream muscles and zebra mussels catched in limnic ecosystems is shown.

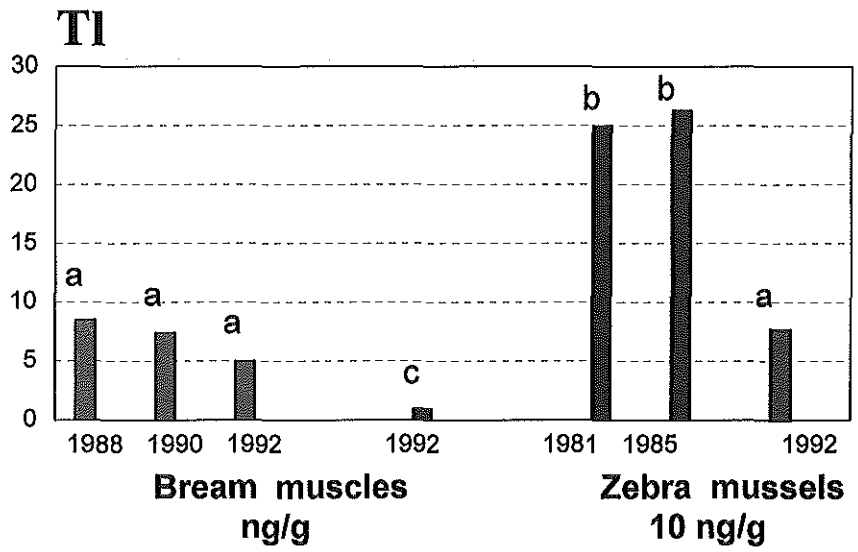


Fig. 6: Thallium concentrations in homogenates of bream muscles and zebra mussels collected in the Lake Constance (a - Konstanzer Trichter; b - Langenargen) and the Lake Belau (c)

Obviously, the mussels are more sensitive bioindicators for Tl than breams. Moreover, the Tl concentrations in biomaterial from the Lake Constance are significantly higher than those observed in the lakeland district of Bornhöved (Lake Belau). It should be noted that such investigations became only possible after developing the sensitive IDMS method mentioned above.

Finally, a result from the long-term rain water program of the Institute is shown in Fig. 7.

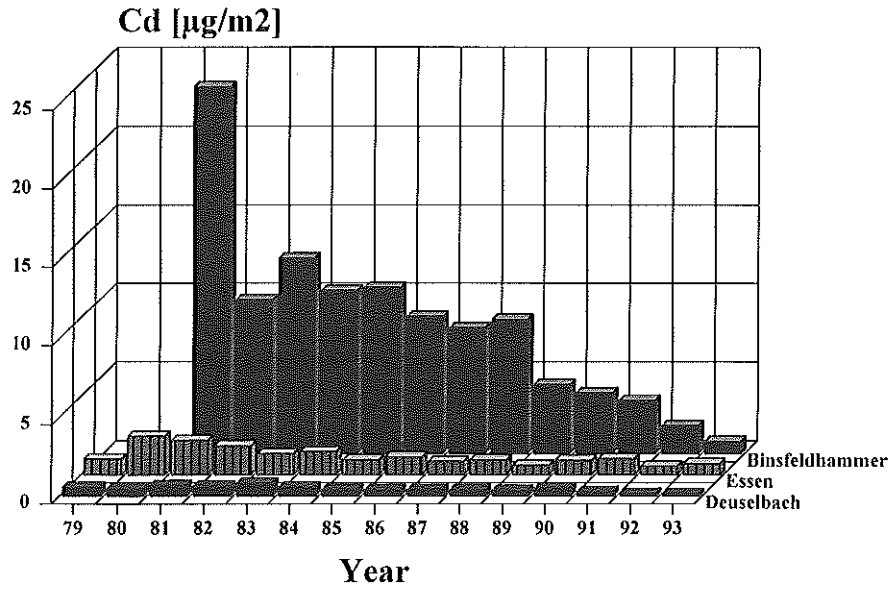


Fig. 7: Wet deposition of Cd (per square meter and day) at different sampling sites between 1979-1993

The wet deposition of this heavy metal analyzed by electrochemical methods demonstrates also the influence of human activities on the environment. The Cd deposition increases from the rural area (Deuselbach) to the municipal area (Essen) and shows its maximum at the industrial site (Binsfeldhammer). At the latter place the introduction of modern exhaust filtration techniques has considerably improved the situation during recent years.

Conclusions

Modern environmental analysis can only be based on multimethod approaches taking into account the merits and problems of current analytical procedures. The most important prerequisite for accurate analysis besides the proper application of state-of-the-art methods and the employment of well-qualified staff consists in the optimized and standardized collection, preparation and storage of suitable samples.

The permanent improvement of the analytical procedures as well as the development of new methods up to the level of standardized protocols for real samples are necessary to

enhance the quality and quantity of information about anthropogenic influences on the environment.

Internal and external quality control has to be performed regularly to ensure reliable analytical data which can be used for environmental modelling, prognostic trend analysis as well as legislative actions.

Acknowledgment

The long-term and careful work of the ESB crew at the Institute of Applied Physical Chemistry is gratefully acknowledged. Financial support was contributed by the Federal Ministry of the Environment, Nature Conservancy and Reactor Safety.

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Organic analytical characterization of marine matrices of the German Environmental Specimen Bank

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Abstract

During investigations on the occurrence and distribution of contaminants in coastal organisms of the North Sea and the Baltic organochlorine compounds such as *hexachlorobenzene* (**HCB**), *octachlorostyrene* (**OCS**), *hexachlorocyclohexane isomers* (**HCH**), *dichlordiphenyl-trichloroethane* (**p,p'-DDT**) and its metabolites, *polychlorinated biphenyls* (**PCBs**), polycyclic aromatic hydrocarbons (**PAHs**) such as *benzo(e)pyrene* or *perylene* and heavy metals such as *mercury, cadmium* and *lead* were determined in selected algae species - bladder wrack algae - (*Fucus vesiculosus L.*), blue mussel (*Mytilus edulis L.*), fish - eelpout - (*Zoarces viviparus L.*) and herring gull eggs (*Larus argentatus L.*).

The sampling network for marine specimen of the German Environmental Specimen Bank (**ESB**) covers the German common wadden sea from the outer estuary of the river Weser - National Park Niedersächsisches Wattenmeer -, the Elbe estuary, the mud flats of the National Park of Schleswig Holstein - Sylt-Römö mud flats between the isles of Sylt (Germany) and Römö (Denmark), the coastal regions of the south-western Baltic Sea - National Park Vorpommersche Boddenlandschaft - and the coastline surrounding the isle of Rügen.

Organochlorine compounds were determined by high-performance liquid chromatography (HPLC) and gel permeation chromatography (GPC) with electron capture detector after sample pre treatment and clean up. Evaluation of the data from the programme made obvious significant geographical differences in the levels and the pattern with regard to the substances involved. For **HCB**, **OCS** and **Hg** a crucial point of contamination within the German Bight (isle of Trischen) was recognized that was apparently influenced to a large extent by the inflow of waters from the Elbe.

Introduction

Contamination of coastal zones, estuaries and adjacent semi-closed marginal seas with potentially harmful inorganic and organic substances is generally most severe in densely populated and highly industrialized regions.

The most important problems of the analysis of e. g. chlorinated biphenyls (**PCBs**) in sea water are depending on the following parameter:

- many other organic compounds with 10^6 - 10^8 higher concentration levels are interferring the detection of the very low concentrations of **PCBs**
- possible contamination with compounds in solvents, glass ware and atmosphere;
- seperation of the PCBs of interest from other compounds, which are interferring the detection by GC-ECD.

It is the intention of the presented study to provide baseline data of persistent, bioaccumulative organic substances (e.g. **HCBs, DDT** and its metabolites, **HCH, HCB** and **OCS**) in marine matrices acting as aquatic bio-indicators of different trophic stages from coastal waters of North- and Baltic Sea which suffer under environmental stress through man's activities. Interests centred upon spatial changes in the contaminant concentration levels, as they might give an indication of the distribution behaviour of the investigated substances.

In order to understand the extent to which aquatic biotops have been influenced by man's activities, it becomes crucial to determine contaminant levels in different aquatic compartments with appropriate analytical certainty (**s. Fig. 1**). Large accumulating rates of 10^9 for concentration of organic pollutants (e.g. **PCB**) in the water column to the highest marine trophic stage - mammals - show the significance of biological marine indicators.

Perusal of the literature over the last decade indicates that insufficient attention has been paid to the quality of data obtained in many cases (s. Fig. 2). Recent intercomparison exercises for trace metals and organochlorine compounds in biological material [1,2] have demonstrated very clearly that the level of agreement between laboratories is still unsatisfying and that many of the analytical methods used to generate data are of doubtful validity. More than two billion DM were spend for wrong analytical data in 1992 [3]. Trace analyses are subject to numerous difficulties including interferences, inappropriate instrumental settings, and uncontrolled gain or loss factors, which can complicate measurements and evaluation and introduce uncertainties in the final results. Accuracy is very difficult to achieve in environmental analyses; yet it is extremely important. The methodological approaches may therefore be also regarded as a contribution to harmonize analytical results with the actual contaminant levels in marine samples. At least to provide possible errors in collection, preparation, analytical clean-up and analytical characterization of matrices, special guidelines (Standard Operating Procedures **SOP**) for all steps are performed in the German Environmental Specimen Bank (**ESB**) of the Federal Government. Al steps are carried out according to these **SOPs** .

Polycyclic aromatic hydrocarbons (**PAH**) result especially from incomplete fossile combustion, wood burning and off-shore waste combustion. Other immission sources are waste gases of industrial and private combustion processes. **PAHs** are ubiquitous in the environment and are important in the assessment of the air quality situation. They accumulate in soil and sediments, because of their long-term stability and a very slow biological decomposition. A number of the **PAHs** have known carcinogenous characteristics. Therefore, their determination is of very high importance.

Experimental

Materials and methods

As mentioned above, the sampling network covers the the German coastline of the North Sea

from the Weser estuary to the Danish border and areas within the limited range of the 10 m low water lines along the German coasts in the Baltic Sea nearly to Polish/German border. Figure **3** provides an overview on all areas investigated within the German ESB project.

Fish

The eelpout *(Zorces viviparus* L.), a catadromus and euryhaline species, which is a sessile fish in the coastal and estuarine regions of the German mud flats was selected for Environmental Specimen Bank (**ESB**) studies. For chemical analysis one age group (total length 18-24 cm) was selected. Samples were taken in spring with a "Hamen" a special net for fishing this species (mesh width 10 mm, 8 m wide). At least 250 specimens were collected in one area. Each fish was dissected with Titanium or quartz-glass knives under clean laboratory conditions in the mobile laboratory of the institute. Liver and muscle of each fish was directly frozen over liquid nitrogen to avoid any changes of chemical compounds.

Herring gull

Eggs of the herring gull (*Larus argentatus* L.) are collected from bird sanctuaries - **Mellum** (Weser estuary), **Trischen** (Elbe estuary) and **Heuwiese** (Baltic Sea). The eggs are collected from breeding colonies with at least 10.000 pairs. Two egg clutches are marked and the second egg is collected for the ESB, when a third egg is laid to the nest. In every breeding colony about 100 eggs are gathered. The eggs are kept cool until egg sampling is completed. Then they are blown with purified argon and the egg contents are frozen over liquid nitrogen.

Blue mussel

In coastal regions of the North Sea, the mud flats of National Park of Niedersachsen and National Park of Schleswig Holstein, mussels are collected during low tide when the mussel beds come up from the water. About 300 individual mussel of 4 - 7 cm size are collected from each region. The water is drained off and the mussels are directly frozen over liquid nitrogen.

Bladder wrack algae

At the same sampling sites as for blue mussel about 2 kg of whole thalli of bladder wrack algae

are collected. Adjacent particles are taken off manually. The algae is washed in sea water of the collection site. After draining of the water the whole plants are frozen over liquid nitrogen.

Air "dust" samples

Air samples are collected in a rural area with low-volume samplers with a modified head. Sample preparation is performed at a flow rate of 1 - 3 m^3/h for a period of 14 days. Flow rate is measured daily. A teflon filter coupled to a precleaned PUF plug with apassage of 50 mm diameter is employed to collect the particulate (dust) and gaseous phases, repectively.

Preparation of biological materials

At the ESB facilities in Juelich all materials are prepared for analytical characterization and long-term storage. According to the SOPs the cooling chain is obtained, e.g. the dissection of mussel tissue is performed under laminar flow box with nitrogen atmosphere at temperatures less than minus 150 C. All materials are ground to a fine powder of less than 200 microns and bottled to 10 g sub-samples which are stored for retrospective analysis in the next decades (s. **Fig. 4**) [4].

Analytical methods for chlorinated hydrocarbons

The individual steps of the entire procedure are shown schematically in the flow scheme given in Figure **5**. The used symbolism [5] coincidentally gives an insight into the applied physico-chemical principles.

The sample material is added to anhydrous sodium sulphate/seasand and mixed in a porcelain mortar. The prepared sample material is than extracted with a n-hexane/acetone mixture in an extraction column. The fat content is calculated from the weight of the dry residue after rotary evaporation of the base extract. After different steps of extraction a gel permeation system (**GPC**) is used for the collection of the **CHC**-fraction (**CHC** = chlorinated hydrocarbons). The high-performance liquid chromatography (**HPLC**) method is the dominant analytical

technique used for investigation of terrestrial-, aquatic- and atmospheric environmental samples.
The detection of organochlorine signals is carried out by capillary gas chromatography equipped with electron capture detector (**ECD**),

The *organochlorine compounds* are determined in *soft tissue* of blue mussel, in *liver* and *muscle tissue* of fish (eelpout) and in homogenized *thalli* of bladder wrack algae by high-resolution silica-fused glass capillary gas chromatography equipped with different detection systems (ECD, FID, etc.) in combination with the above mentioned sample pre treatment [6].

Analytical methods for polycyclic aromatic hydrocarbons
The quantitative separation of toxic polycyclic aromatic hydrocarbons (**PAHs**) is commonly performed by high resolution gas chromatography (**HRGC**): PAHs with flame ionization detector (**FID**) [7] or by high-performance liquid chromatography (**HPLC**) with UV- and fluorescence detector (**UVD, FD**) [8] or electron capture detector (ECD) [9,10,11]. Gas chromatography-mass spectrometry for quantification is applied to all methods. A special sample pre treatment for atmospheric compounds ("dust") [12] is schematically given in Figure 6. The HPLC-separation is done with silica-gel column.

As mentioned above most of the polycyclic aromatic hydrocarbons (**PAHs**) is originated from incomplete fossile burning. The largest part introduced to the sea is the pathway via atmoshere. Collection of "dust" samples with a low-volume sampler are investigated in a rural area (Juelich). The determination of this "dust"-samples show a significant pattern (s. Fig. 7). The determination of **PAHs** bounded to atmospheric particles is important because this compounds are accumulated in marine organisms (e. g. blue mussel tissue).

Future investigations are stressed to the modification of the separation pre treatment, which is necessary for good selectivity of polycyclic aromatic hydrocarbons in biological matrices.

Results

Generally, the ratio between α- and β,-**HCH** varied from about 1:0.5 to 1 :0.8 in the Baltic sampling stations (s. Fig. 8). Although the β-isomer is a minor constituent of technical HCH it deserves still some attention. **β-HCH** was clearly discernible in some of the chromatograms of blue mussel samples of the Baltic Sea, while it was below the detection limit in samples of the collection sites surrounding the coasts of the isle of Ruegen. Significantly enhanced **β-HCH** concentrations occurred only in the material collected from the Strelasund (possible high industrial polluted waste waters (location 8, s. Fig. 8)).

HCB (hexachlorobenzne) is no longer introduced into the environment in larger amounts, because its use as fungicide is banned. However, it still appears as by-product of many chlorination processes and the HCB-contamination of rivers and the sea might be derived from such activities. Most of the investigated blue mussel samples from the Baltic Sea coast show concentration levels from 0.02 to 0.2 ug/kg fw for HCB (s. Fig. 9). Blue mussel samples collected from 1985 to 1990 in the North Sea mud flats show the same concentration levels with a decrease within the years (s. Fig. 10). Earlier investigations reported in literature [13] showed that fish samples from the Elbe on its lower course between the city of Hamburg and its mouth near Cuxhaven were significantly contaminated with respect to this substance. Data gained during a newer study of the same authors [14] confirmed that the Elbe obviously contributes to a large extent to the HCB-contamination of adjacent marine waters.

High PCB concentrations (polychlorinated biphenyl) are obtained in the herring gull eggs from the bird sanctuaries Trischen and Mellum. Possibly, the high concentration of PCBs are the reason of low nest success, depending on egg shell crack. After closing of industries and municipal wastes upstream the river Elbe in 1990/91 (after the reunion of FRG and GDR) a sharp decrease of **PCB** and mercury concentration is obtained (s. Fig. **11** and Fig. **12**). Correlated to this, the thickness of egg shells is increasing (s. Fig. **13**).

The evaluation of **PAHs** in air-dust samples of 1992 in a rural area shows that **benzo[e]pyrene (BeP)** a typical seasonal variation with high concentrtaions in winter and low concentrations in summer. Most of the other **PAHs** are following the same trend as shown for **BaP** (s. fig. 7). Only **benzo[a]anthracene** and **benzo[a]pyrene** show significantly lower concentrations in summer, possibly depending on photochemical or chemical (electrophilic) reduction processes. These processes are depending on higher sunbeam or photochemically produced agents like NO_x or **ocon,** respectively. Future investigations have to be carried out on concentrations and reactions to biological matrices of the terrestrial or aquatic environment.

Discussion

Data generated during the present study supported the impression that compound-specific differences in the concentration levels existed between the North Sea and the Baltic Sea. This was most obvious for some of the chlorinated hydrocarbons. They showed higher levels in samples of the Baltic Sea. It is most probable that diffuse inputs of the various substances and the prevailing hydrographic conditions in the Baltic Sea might lead to the rather uniform contamination situation within its coastal areas studied.

In contrast, the data of the North Sea indicated considerable differences in the contamination levels along the coastal areas between the Weser estuary and the Elbe estuary,. It seemed that the observed structured distribution of substances was to a large extent influenced by the inflow of waters from the river Elbe and the prevailing residential currents in the German Bight [15,16]. Apart from the significance of hydrographic conditions an explanation for the spatial changes of the contaminant pattern may be found in specific differences in the mobility of each single compound in the aquatic environment [17].

Regarding organochlorine compounds, one may assume that depending on certain physico-

equilibrium will tend to be established between detectable concentrations in fish and amounts distributed between the different compartments of the aquatic medium. On this basis one would expect the more volatile and more water soluble substances (typical examples are **α-HCH** and **p,p'-DDE**) to reach the more distant waters. Other substances with lower volatility and water solubility (i.e. **β-HCH** and **p,p'-DDD**) will show a minor tendency to be transported over longer distances. Results comming from literature confirm these assumptions.,

Figures

Fig. 1: Accumulation of PCB in marine matrices

Fig. 2: Decrease of published concentration values of Cd in sea water within the last 30 years depending on better sampling techniques and new detection methods with high accuracy

Fig. 3: Selected areas for the German Environmental Specimen Bank (ESB) of the Federal Government

Fig. 4: Flow scheme of the sample preparation steps for chlorinated hydrocarbons determined in the German ESB

Fig. 5: Flow scheme of the clean-up procedure for the detection of chlorinated hydrocarbons

Fig. 6: Sample pretreatment for the separation of polycyclic aromatic hydrocarbons in air samples

Fig. 7: Seasonal variation of polycyclic aromatic hydrocarbons (e. g. BaP) in air samples collected in a rural area

Fig. 8: α- and β-HCH in blue mussel tissue collected at the German coasts of the Baltic Sea and isle of Ruegen

Fig. 9: Spatial variation of HCB in blue mussel tissue from the Baltic Sea

Fig. 10: Variation of chlorinated hydrocarbons in blue mussel tissue collected from the German mud flats of the North Sea from 1985 to 1990

Fig. 11: Temporal distinction of mercury concentration in herring gull eggs of Trischen (Elbe estuary)

Fig. 12: Temporal distinction of chlorinated hydrocarbons in herring gull eggs of Trischen (Elbe estuary)

Fig 13: Increase of shell thickness of herring gull eggs

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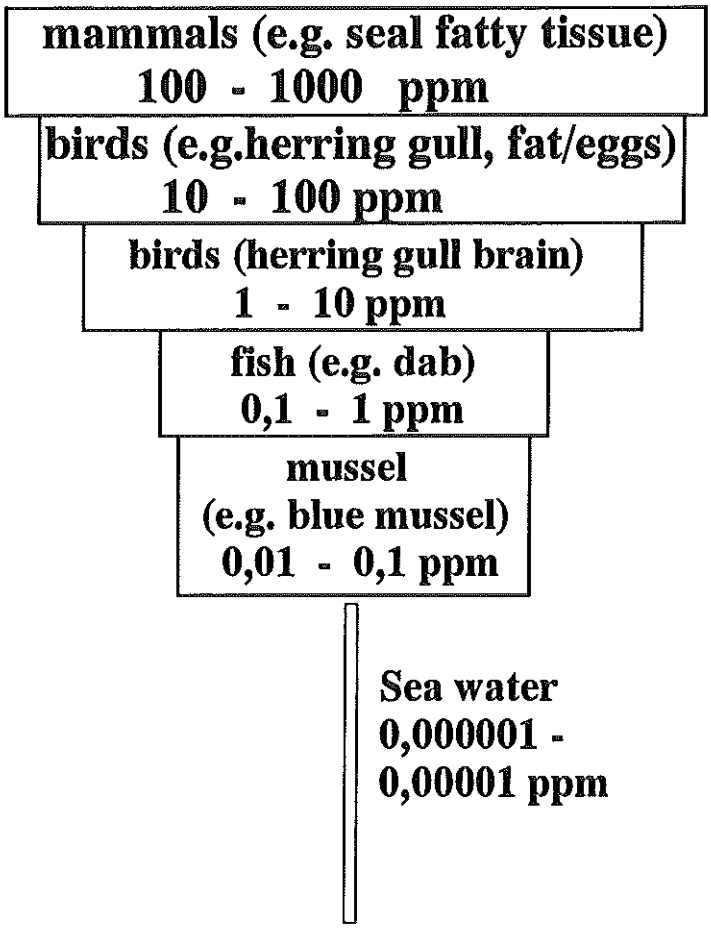


PCB food limit value for fish in the U.S. :
< 2ppm

Fig. 1: Accumulation of PCB in marine matrices

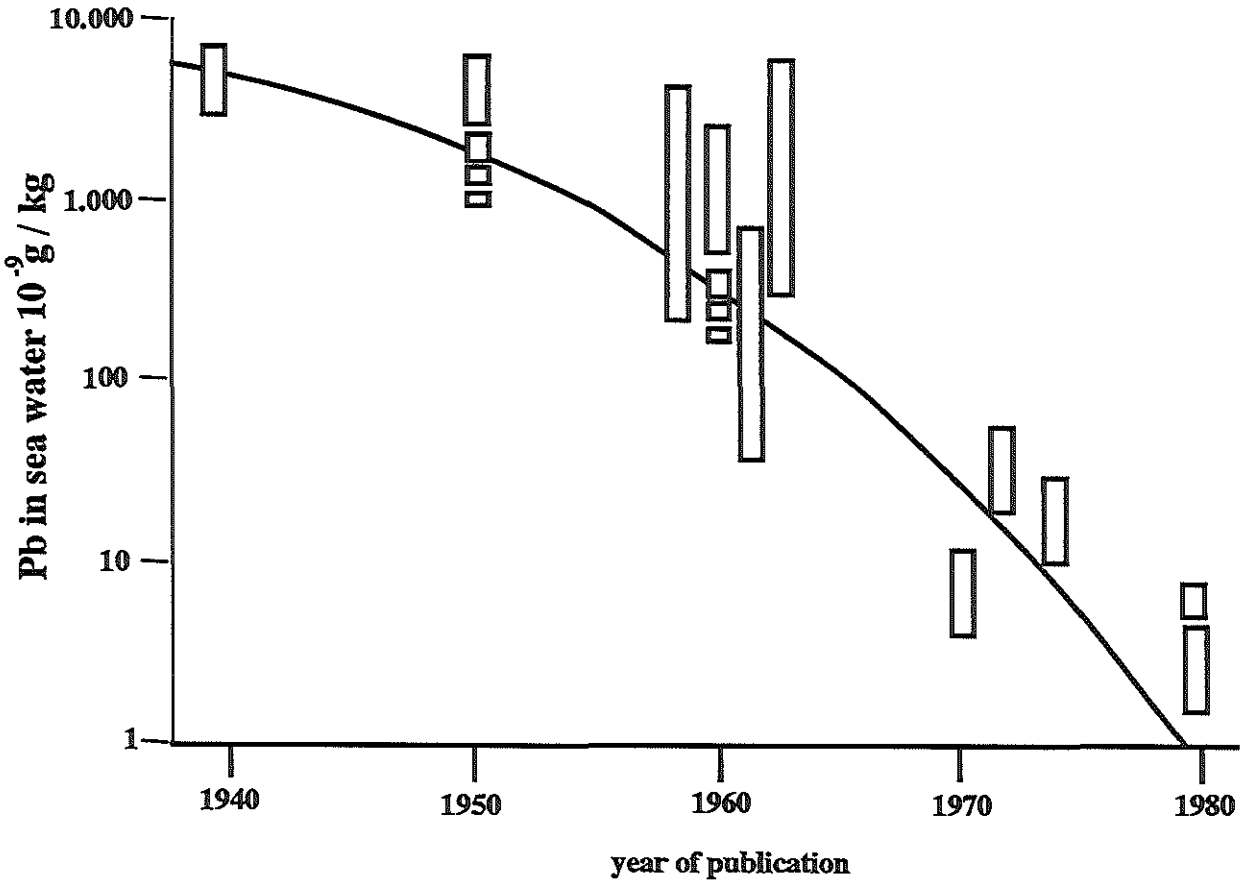


Fig. 2: Decrease of published concentration values of Pb in sea water within the last 30 years depending on better sampling techniques and new detection methods with high accuracy

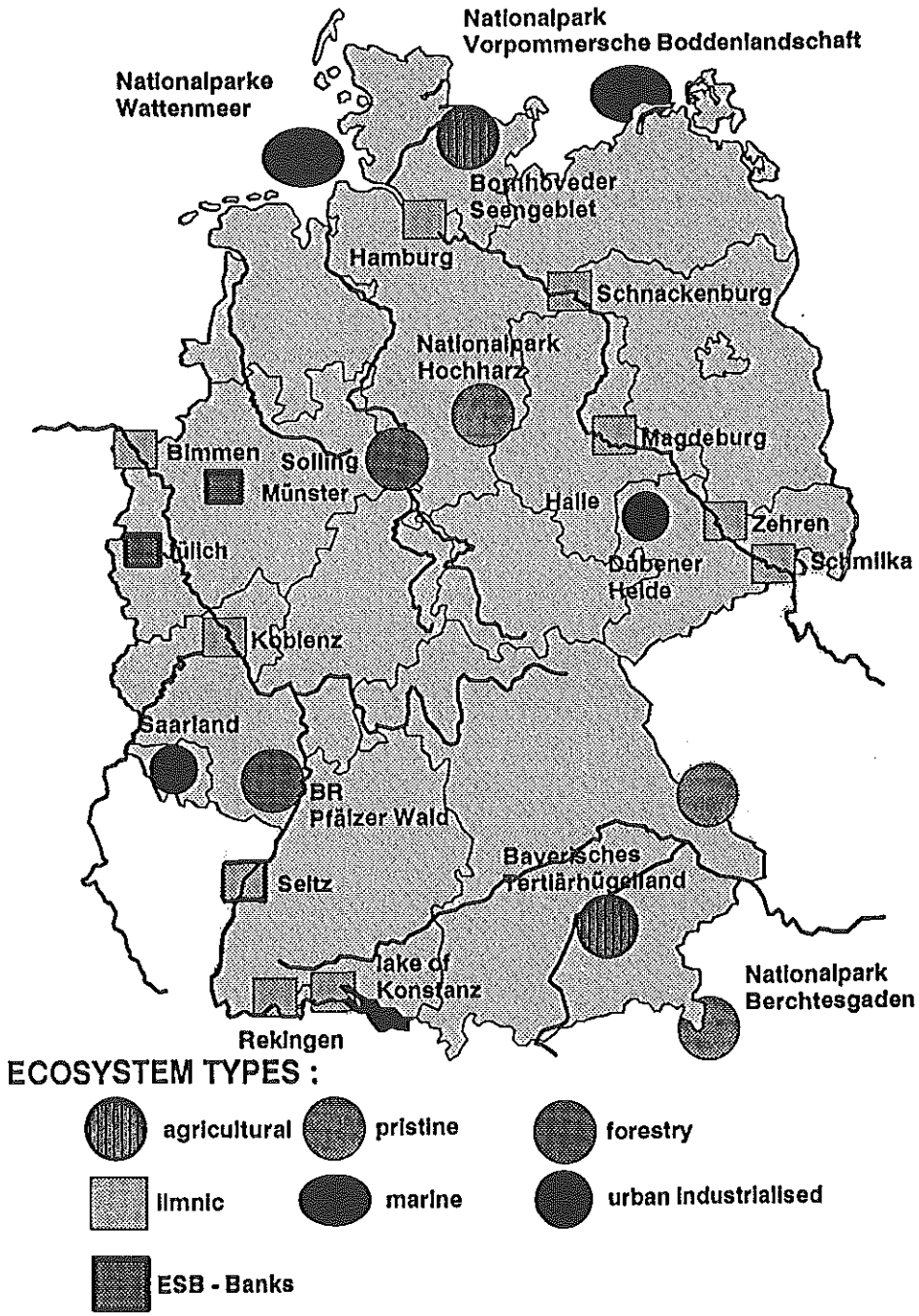


Fig. 3: Selected areas for the German Environmental Specimen Bank (ESB) of the Federal Government

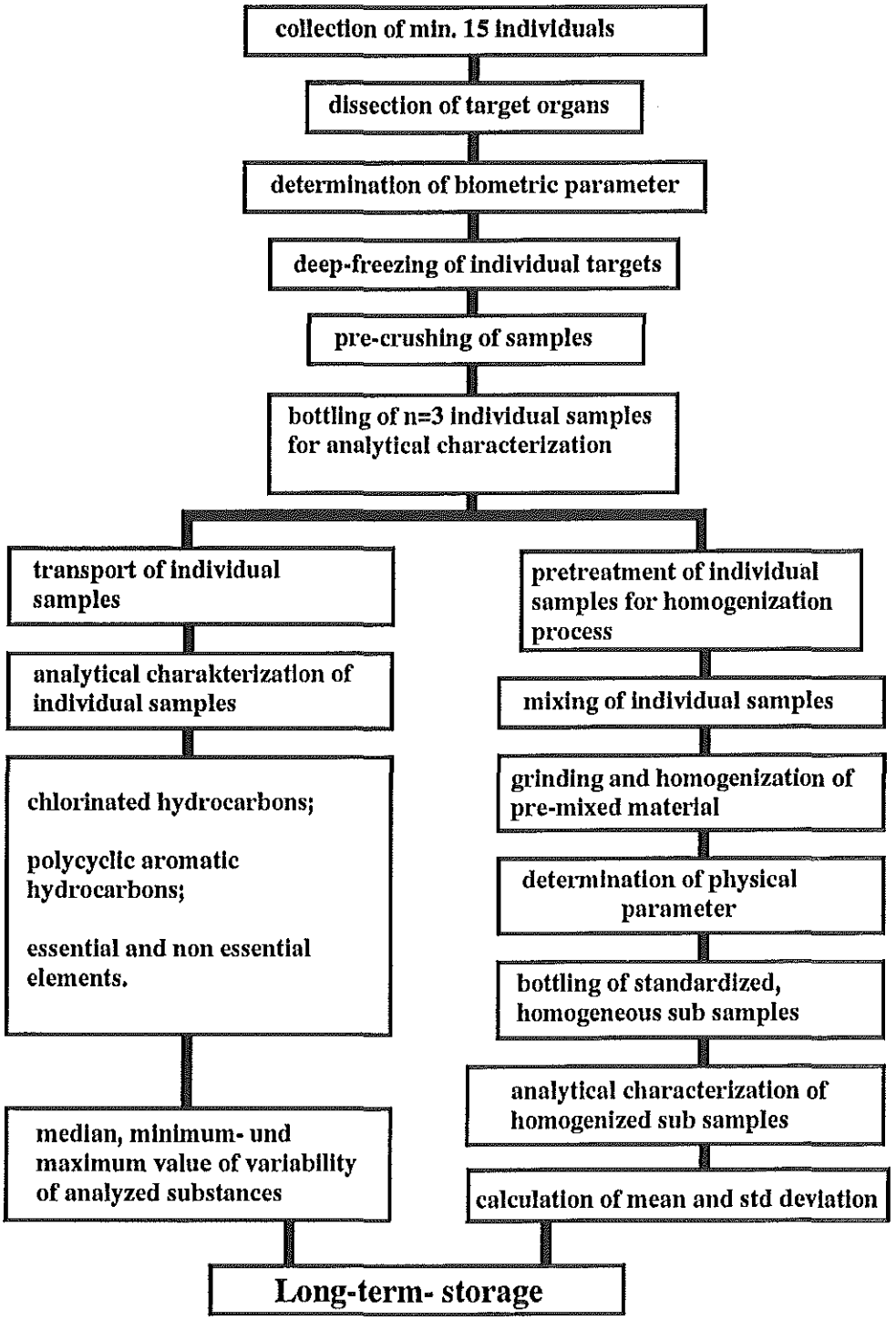


Fig. 4: Flow scheme of the sample preparation steps for chlorinated hydrocarbons determined in the German ESB

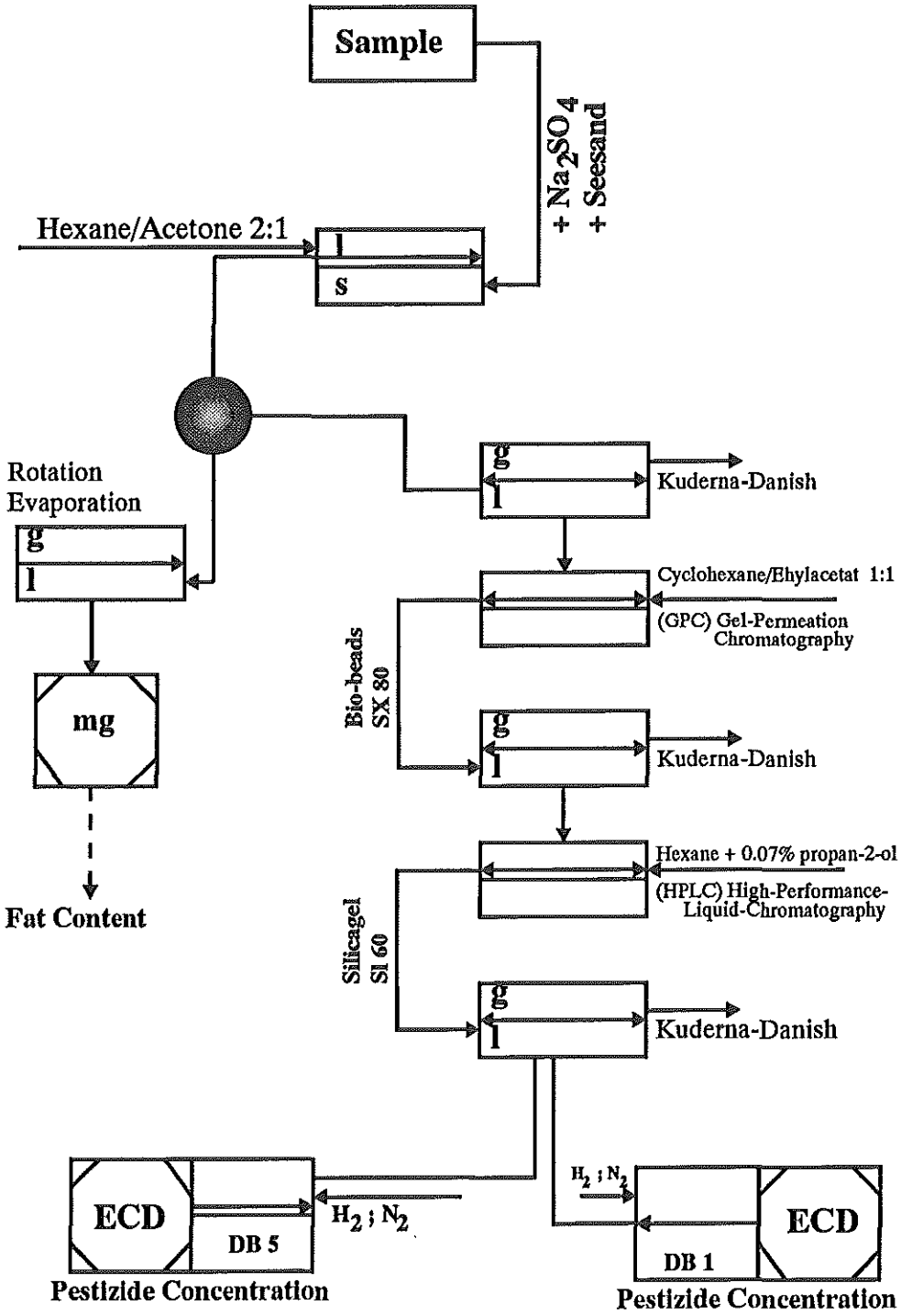


Fig. 5: Flow scheme of the clean-up procedure for the detection of chlorinated hydrocarbons

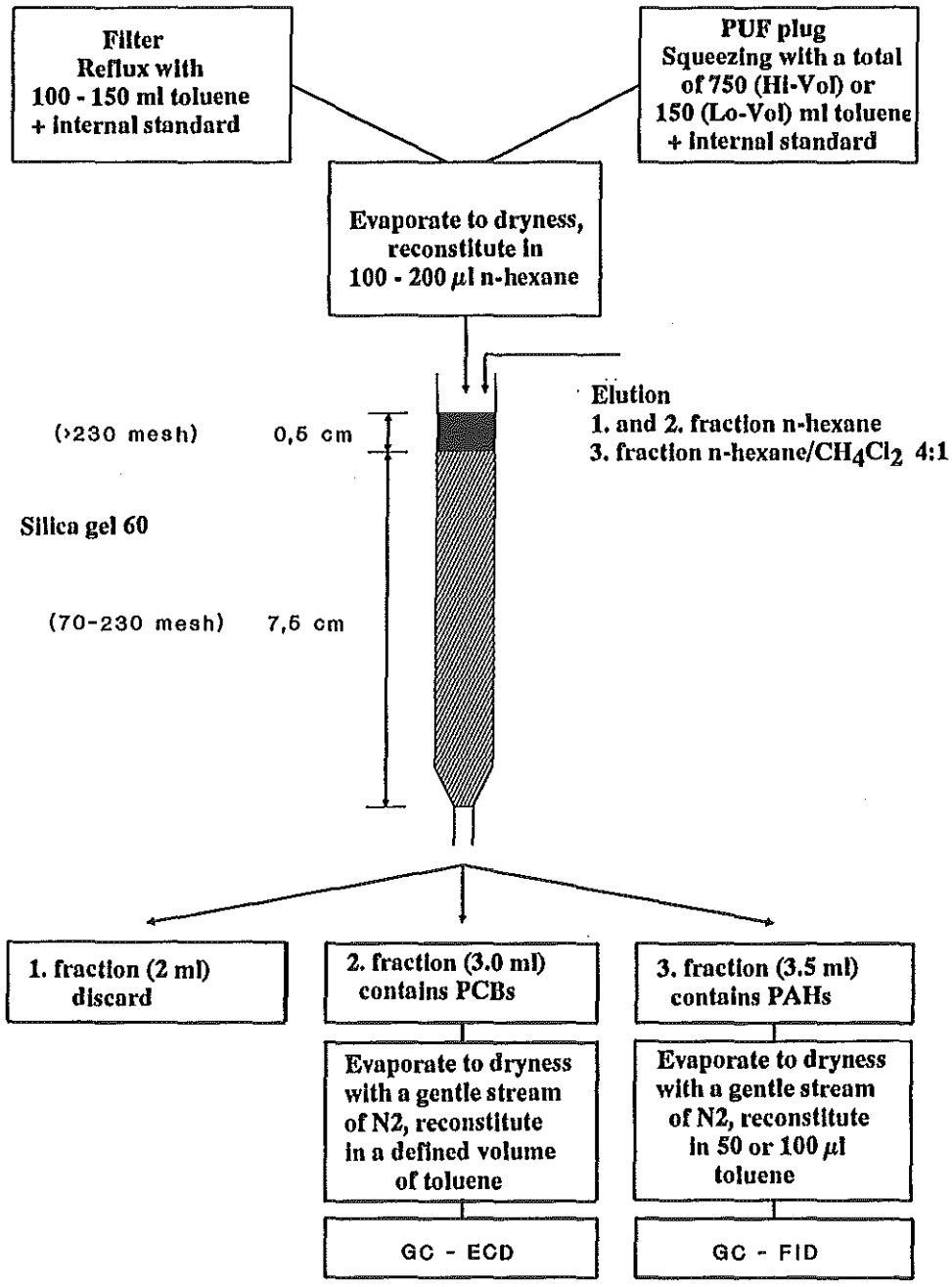


Fig. 6: Sample pretreatment for the separation of polycyclic aromatic hydrocarbons in air samples

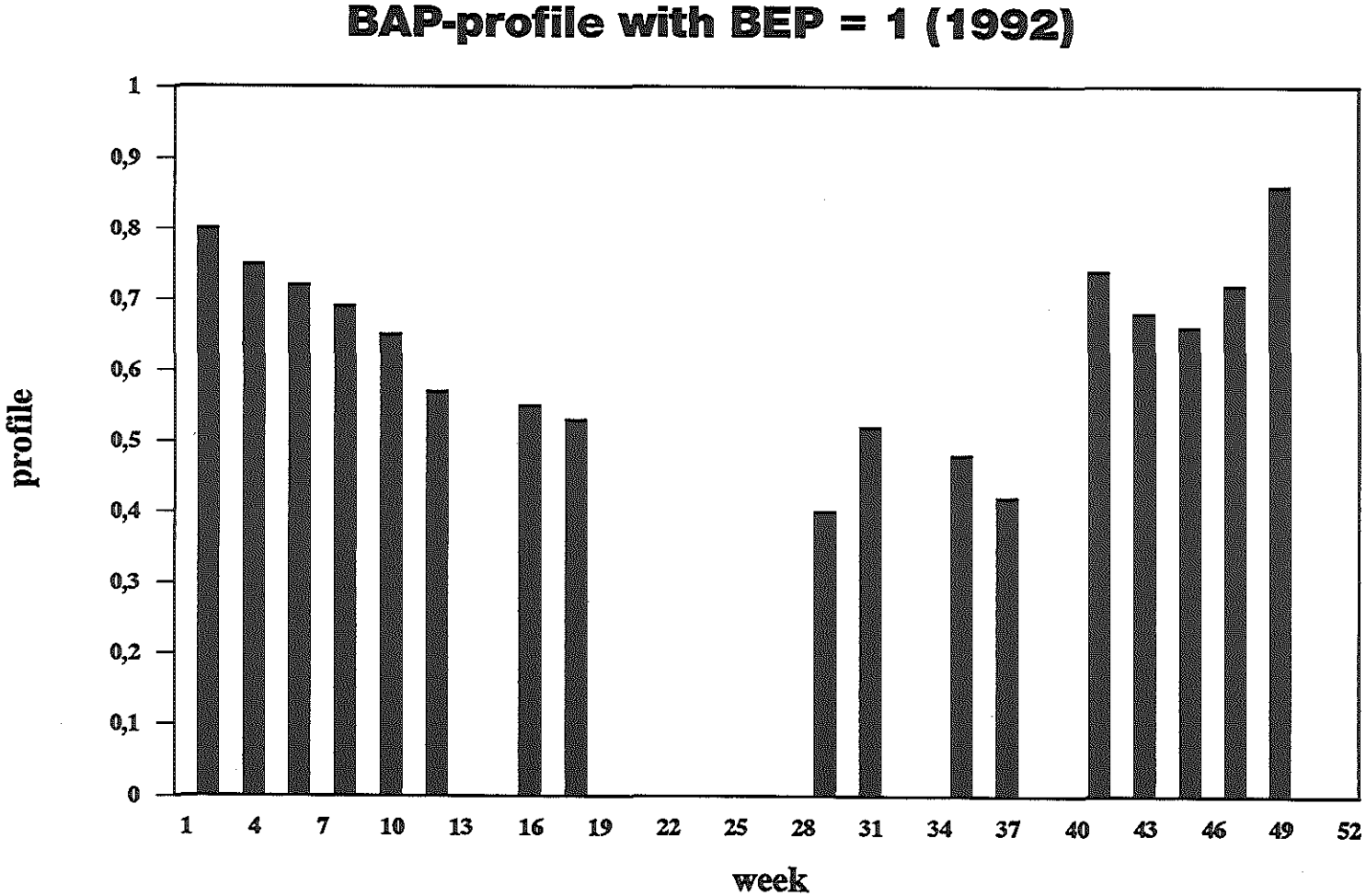


Fig. 7: Seasonal variation of polycyclic aromatic hydrocarbons (e. g. BaP) in air samples collected in a rural area

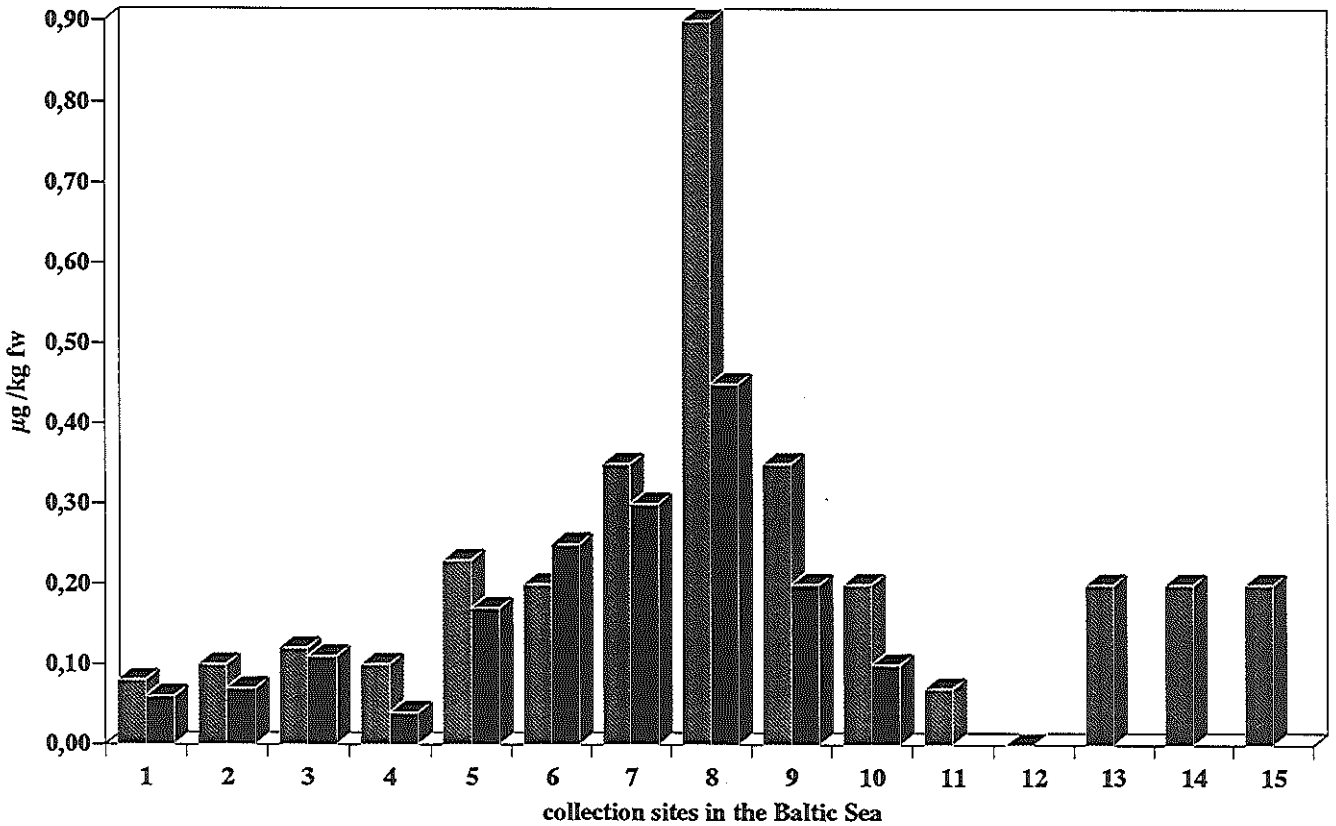


Fig. 8: α- and β-HCH in blue mussel tissue collected at the German coasts of the Baltic Sea and isle of Ruegen

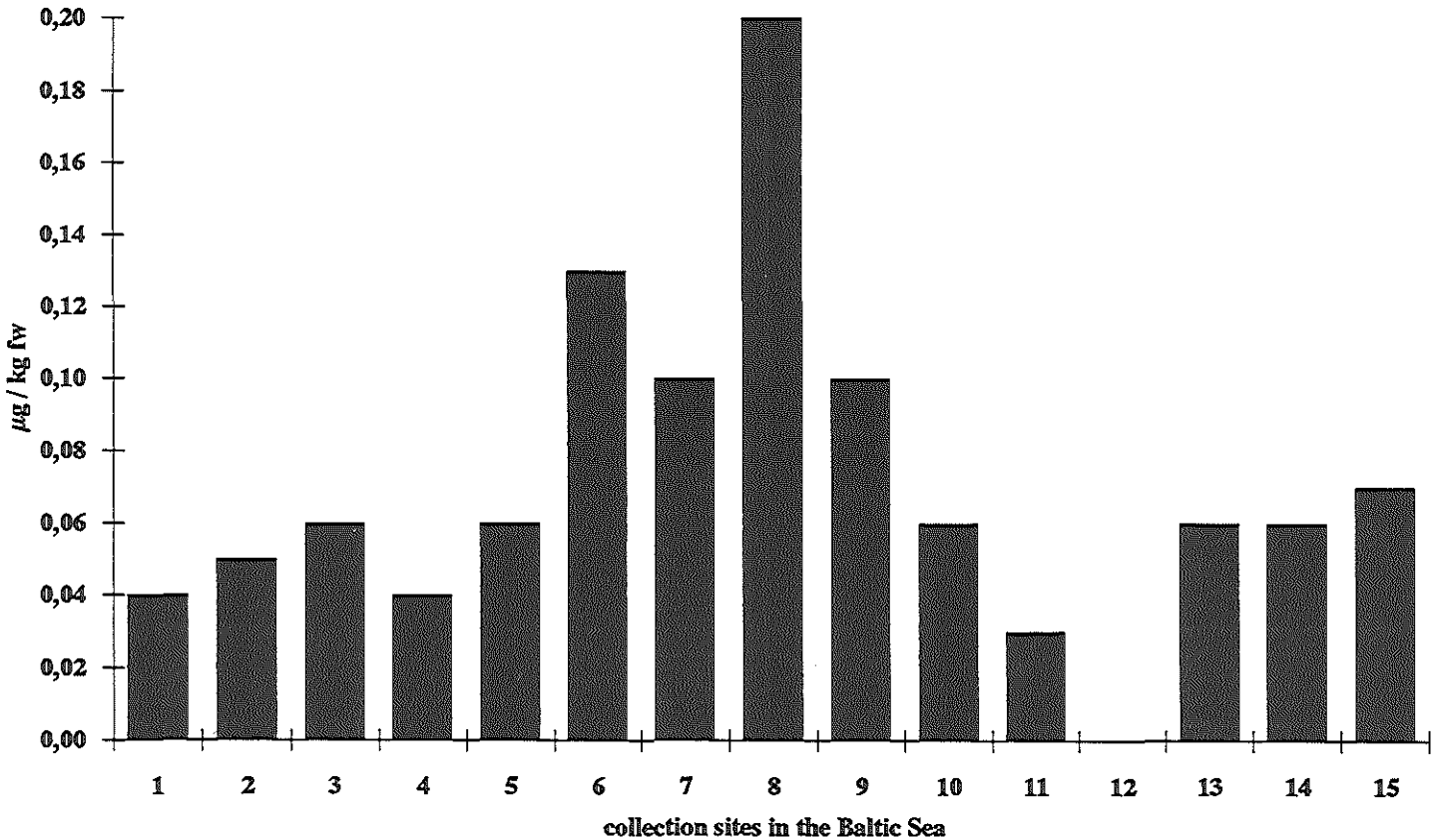


Fig. 9: Spatial variation of HCB in blue mussel tissue from the Baltic Sea

chlorinated hydrocarbons in blue mussel tissue (Mytilus edulis L)

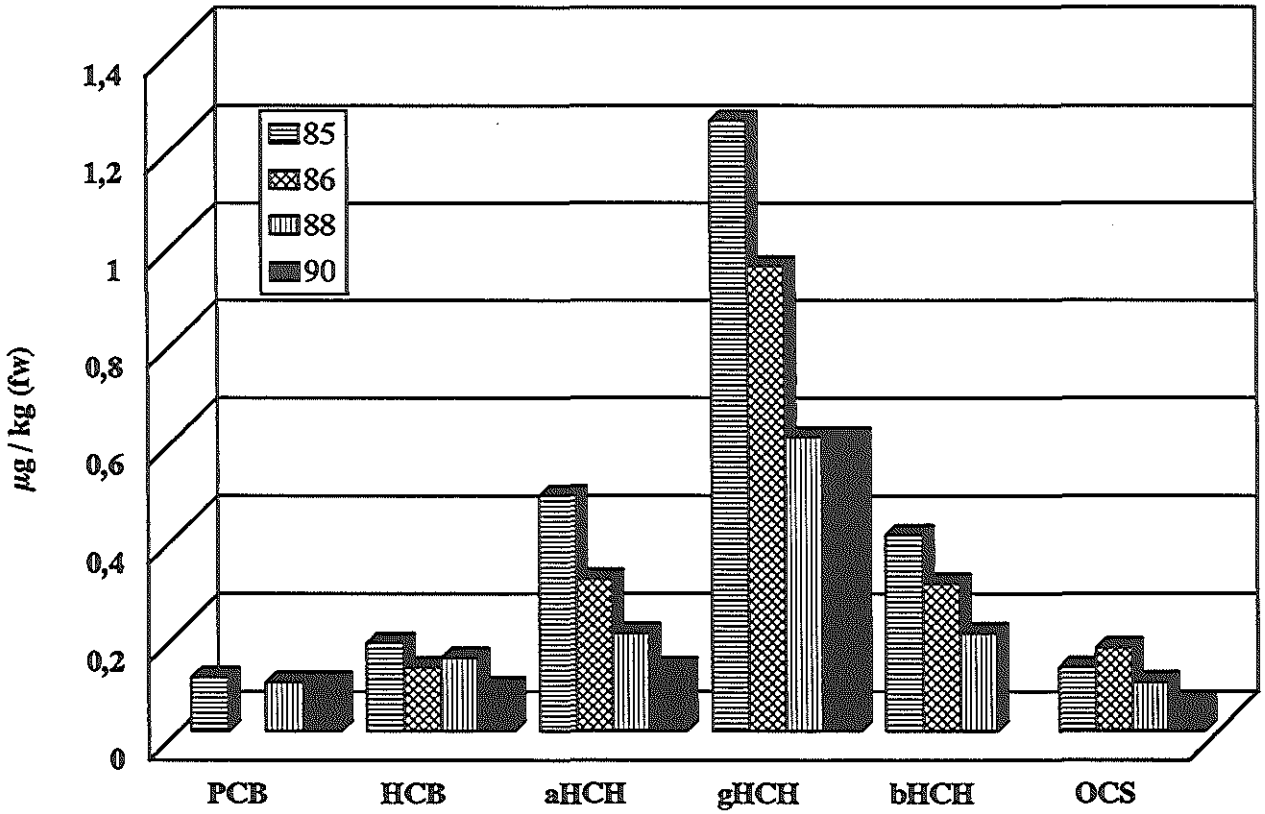


Fig. 10: Variation of chlorinated hydrocarbons in blue mussel tissue collected from the German mud flats of the North Sea from 1985 to 1990

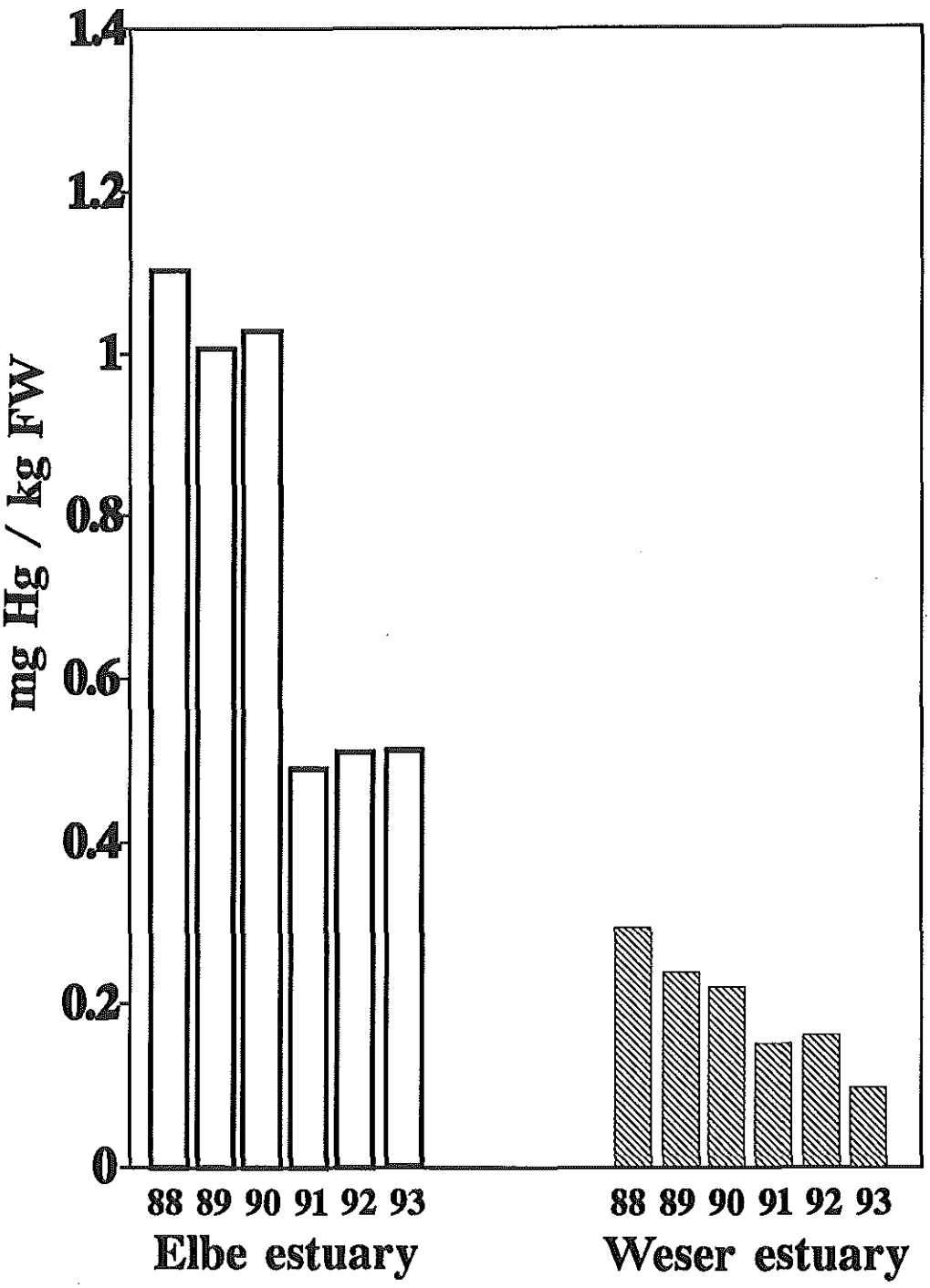
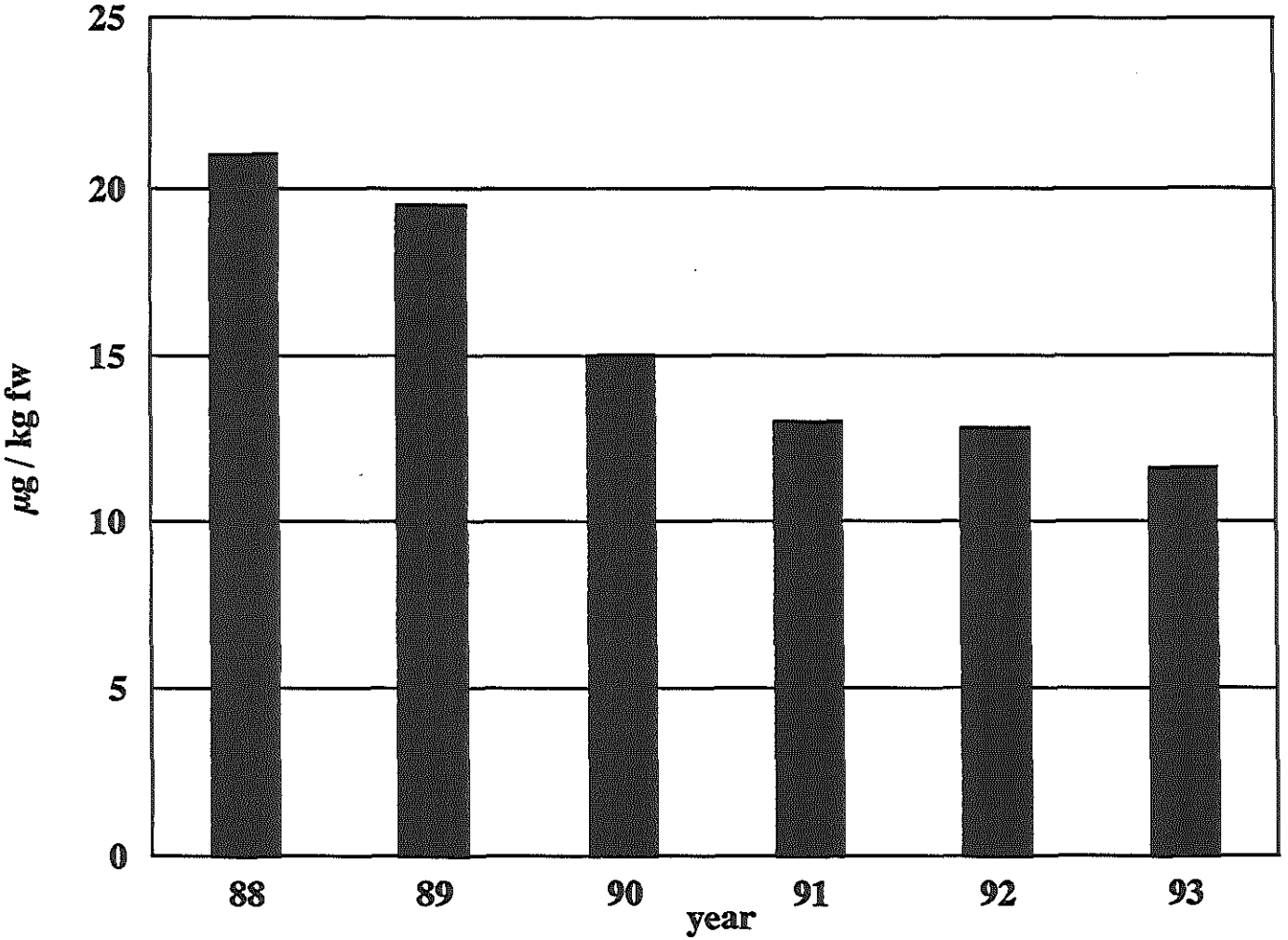


Fig. 11: Temporal distinction of mercury concentration in herring gull eggs of Trischen (Elbe estuary)



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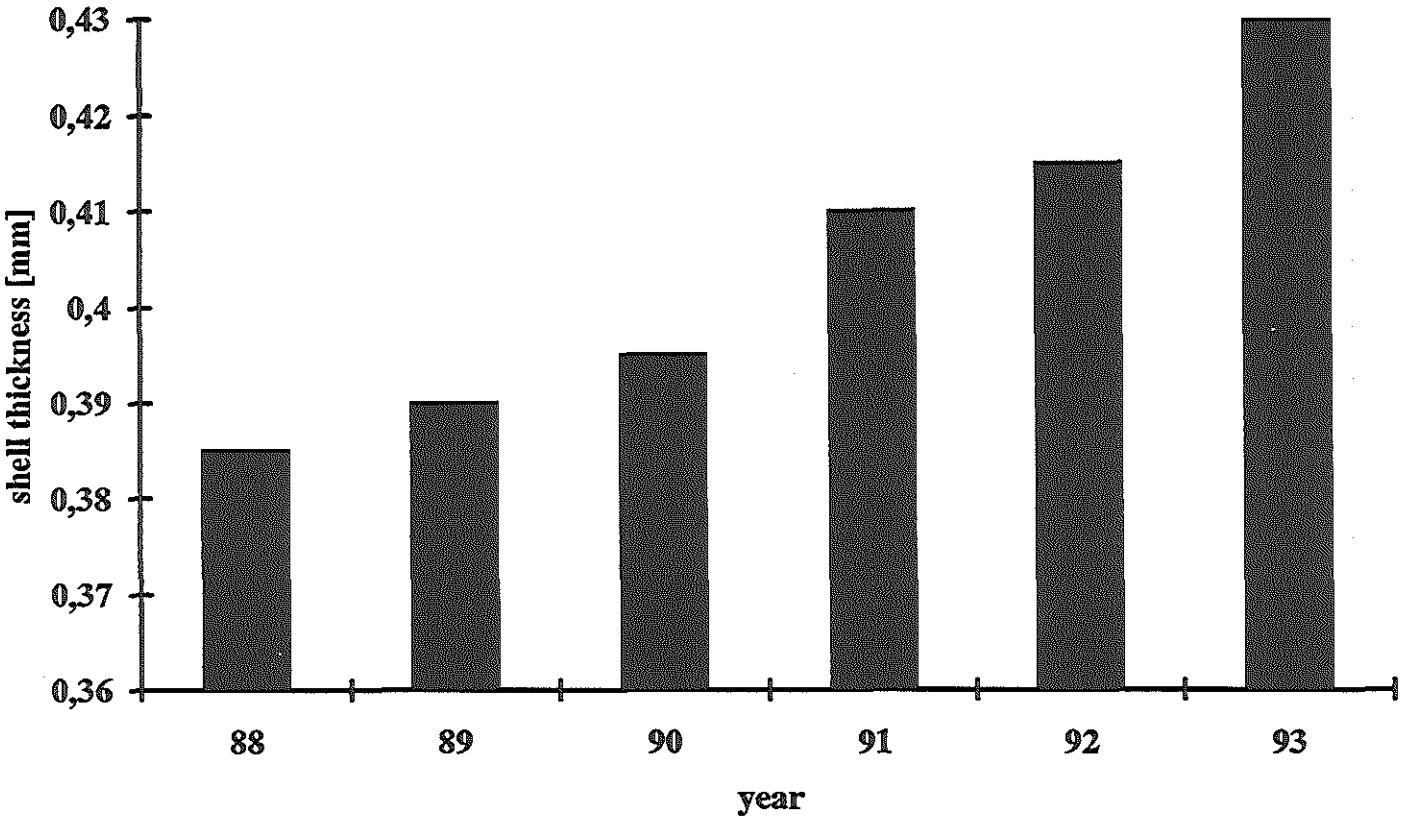

Fig 13: Increase of shell thickness of herring gull eggs

Comparative Analysis of Water and Sediments from Fresh Water Compartments in Egypt and Germany

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Abstract

A comparative study of the distribution of trace elements in the Naser Lake, Lake Constance (Bodensee), and the River Elbe was carried out. The concentrations of more than 20 elements in water and sediment samples were determined using Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and electrochemical methods. The data shows that most of the heavy metals in Naser Lake are comparable with the minimum values measured in Lake Constance and the River Elbe. Elements such as Ca, Cr, Fe, Ni, Zn, Sr, Ba, and Hg illustrate this clearly. Therefore, the area of Naser Lake could be used to establish background data of a pre-industrialized area to monitor any further contamination due to the growing industry.

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Introduction

There is considerable interest in trace element concentrations in the environment for a variety of reasons including their role in health, nutrition, and environmental pollution.

Since the industrial revolution, the effort of removing man-made pollutants from the natural environment has been unable to keep pace with the increasing amount of waste materials and a growing population that further aggravates the situation. This has often resulted in the transformation of lakes, rivers and coastal waters into sewage depots where the natural biological balance is severly upset and in some cases totally disrupted (1).

For the evaluation of the present status of our environment with respect to hazardous chemicals and toxic elements, base-line data from pre-industrialized areas would be desirable. The area of Naser Lake was chosen for this study because of its importance as the main water reservoir in Egypt and for being an un-industrialized area until now.

Therefore, a systematic monitoring of this huge water body seems to be mandatory collecting environmental samples from the lake and establishing a small scale Environmental Specimen Bank in Egypt.

The German Environmental Specimen Bank (ESB) concept which has been continuously developed for more than 10 years implies the installation of an archive for representative environmental samples and their characterization. It is a highly developed, interdisciplinary and long-term project for the national assessment and monitoring of environmental impact from human activities. The diversity of tasks and duties of the ESB requires the collaboration with many institutions in the country and abroad. This study reflects one phase of this collaboration as an example, namely the comparison between certain trace element concentrations in Naser Lake, Lake Constance and the River Elbe.

General features of Naser Lake

The chemical composition of natural waters results from different environmental factors operating simultaneously but with differing influences and efficiency (2): the soil and rock composition, climatic conditions (rainfall, temperature), flora and anthropogenic influences. With regards to these factors, it was necessary to take into consideration the general features of Naser Lake. Naser Lake extends along 500 km of which 300 km are within the Egyptian territory with a median width of about 10 km. According to the hydrological regime of the lake, about 95 % of the sediments carried by the annual flood rest in the southern sector of the lake within the Sudanese borders where the width of the lake ranges between 1 to 2.5 km (3).

The River Nile after passing the second cataract at Wadi Halfa enters the Egyptian territory taking a north eastern course cut in the Nubian sandstones formation. The northern

part of the lake at El-Alaki area has an average width of about 12 km and extends up to 50 km at the eastern side of El-Alaki valley. Within the Egyptian borders, the water in the lake is considered to be stagnant since the average speed is about zero.

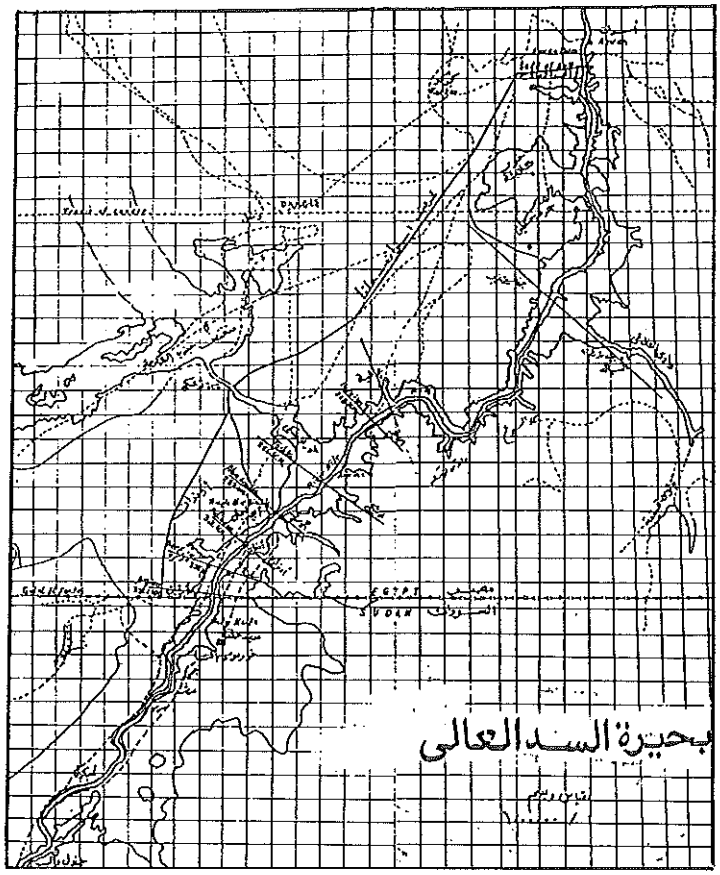

Fig . 1. Map of Naser Lake

Methods and Materials

- Sample collection and preparation :

Samples were collected from 8 sites along the Naser Lake starting from the High Dam and ending at the Egyptian borders as shown in Fig. 1.

Water samples were collected from three different depthes using a Russian water sampler (Malshive). For each sample a minimum of 10 L water was collected, acidified to pH less than 2 and filtered with 0.45 μm millipore filter directly after the arrival to the lab (4). The volume of the filtrate was reduced to 1 L by gentle evaporation.

Sediment samples: A variety of devices are available for the collection of marine sediments by coring, grabbing or dragging. In this study the grabbing method was used to study the

superficial layer of sediment (1-5 cm). All samples were air dried and sieved with 2 mm mesh sieves. For ICP-MS measurements, the sediment samples were digested in pure nitric acid at 180 C° (under pressure), while for INAA the samples were used without any treatment .

Instrumentation

Instrumental Neutron Activation Analysis (INAA):
INAA was used for the analysis of sediment samples. More than 20 elements in sediment samples including Ba, Ta, Eu, Zn, Zr, Ni, Hg, Tb, Th, U, Cs, Se, Co could be determined. The irradiation of the sediment samples was performed at the FRG 2 reactor at Geesthacht for 10 h at 5 . 10^{13} n /cm ^{2} . After reasonable time of decay, samples were counted from 5000 s to 50000 s on a well-shielded HPGe detector (20% efficiency).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Stripping Potentiometry:
For the analysis of water samples ICP-MS was used as a multi-element technique to determine more than twenty element such as Ca, Sc, Ti, Cr, Co, As, Se, Br, Sr, Zr, Ag, I, Sb, Cs, Sn ,Pb and Eu.

Potentiometric Stripping Analysis (PSA) with a mercury film electrode was used to determine the concentration of Pb, Cd and Cu in these water samples.

Results

The distribution of Cd, Pb and Cu in water sample along Naser Lake, obtained by using electrochemical methods, is summerized in Table 1. The Cd concentration ranged between 0.01 - 0.14 µg / L with an average of 0.085 µg / L while the concentration of Pb and Cu ranged between 4.5 - 33.6 µg / L with an average of 18.3 µg / L and 1.9 - 14 µg / L with an average of 7.2 µg / L, respectively .

Location	Cd (ppb)	Pb (ppb)	Cu (ppb)
High Dam	0,011	23,5	8,8
Garph Housin	0,13	10,9	7
Afia	0,14	30,8	14
Abrim	0,13	10,9	9
Toshka	0,06	13,8	1,9
Abu-Simble	0,13	18,6	4,7
Adindan	0,05	4,5	5,8
Sarh	0,03	33,6	7,1

Table 1. Distribution of Cd, Pb, and Cu in water samples from Naser Lake.

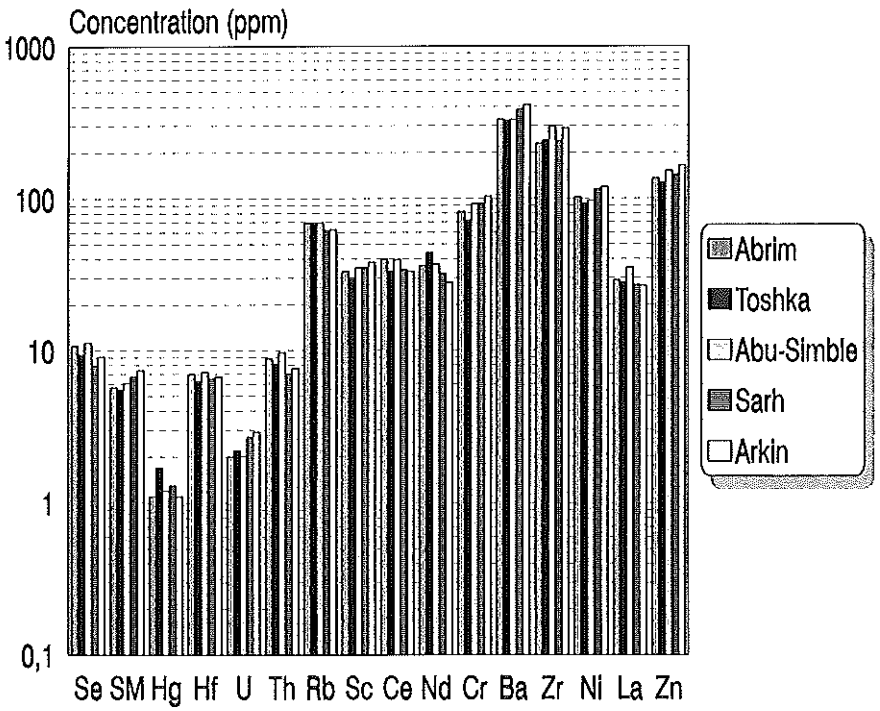

Fig.2. Elemental distribution in sediment samples along Naser Lake.

Fig. (2) shows the concentration of heavy metals in shore and bottom sediments collected from the same sites as the water samples determined by INAA.

The results of many of the anthropogenic as well as the lithopogenic elements are also given.

Metals belonging to the first group Cr, Zn, Ni and Se show average concentrations of 68.4, 104, 105.2 and 9.68 μg /g of dry weight, respectively.

From the second group metals as Sr, Rb, and Zr show an average concentration of 206.5, 66.6, and 258.8 μg / g, respectively .

Elements	Granitic rock	Sandston	Abu-Simble	Arkin
Sb	0,2	0,04	0,385	0,44
U	3	0,45	2	2,9
Se	0,05	0,05	11,3	9,1
Cr	22	35	92,2	103
Ba	420	190	330	411
Sr	440	20	245	229
Zn	60	16	152	164
Zr	15	2	298	289
Hg	0,08	0,03	1,13	0,98

Table 2. Concentration of minor and trace elements in different geological formations .

The concentration of premordial radionuclides U and Th ranged between 2 - 5.5 µg / g with an average of 3.1 µg / g and 2.1 - 15 µg / g with an average of 10 µg /g, respectively .
Fig.(3) illustrates the distribution of Cr, Zn, Ni and Se at different sites along Naser Lake and shows a trend with the highest concentrations at the two sites Abu-Simble and Arkin.

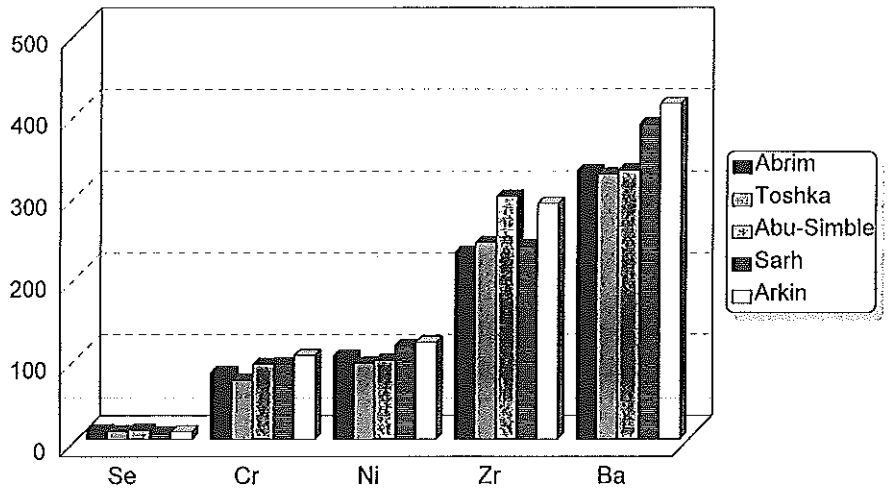

Fig.(3) The distribution of Cr, Zn , Ni and Se at different sites along Naser Lake.

Fig. (4) shows the distribution of Cr, Ni, and Hg within the Naser Lake, the Lake Constance and the River Elbe.
Table (2) summarizes the concentration of minor and trace elements in different geological formations as granitic rocks and sandy sediments in µg / g (5).

Discussion

It is somehow problematic to establish global mean values for the individual trace elements in inland waters, especially in rivers. This could be, in the first place, due to the variety of rock formations and the fluctuation in water transport. However, the concentration of three of the most important pollutants in water Cd, Pb, and Cu were studied. The average content of Cd in these water samples agrees with the background content of Cd in fresh water, 0.07 µg / L (6). Boyle and Edmond (7) found Cu variations greater than a factor of three (0.56 - 0.185 µg / L) in surface water across the antarctic Circumpolar currents south of New Zealand.
Trefry and Presley (8) found that the background content of Pb in fresh water is 0.2 µg / L.

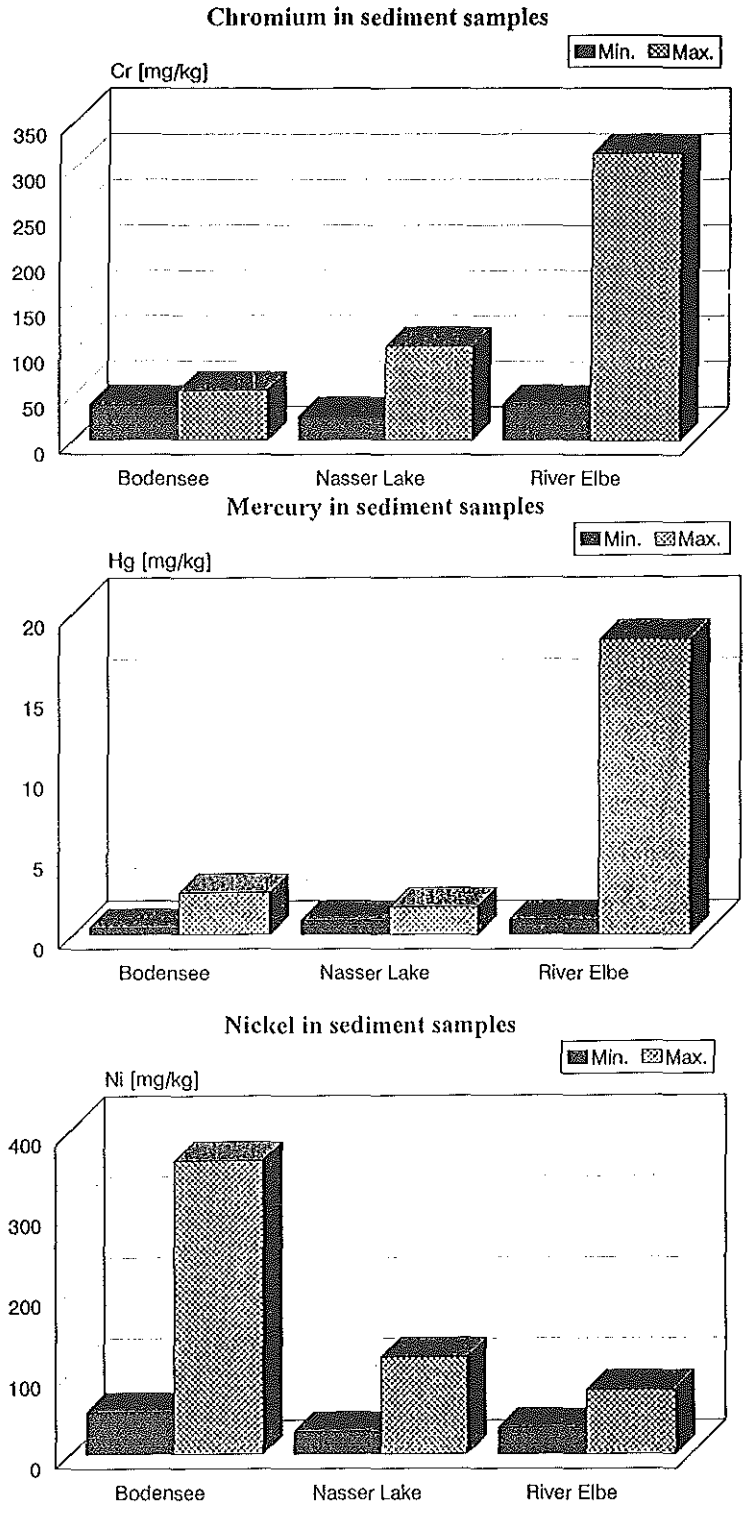

Fig.4. The distribution of Cr, Ni, and Zn in Naser Lake, Lake Constance, and the River Elbe.

A comparison of these background values shows that the values obtained from Naser Lake are enriched by factors between 10 (Cu) and 20 (Pb). This should not be considered as contamination, since most of the trace elements are showing low concentrations when compared to that in the Lake Constance and the River Elbe. These elevated values could be referred to the sample treatment, where samples were acidified before filtration and leaching of trace elements from the suspended matter is most probable.

Trace metals in recent sedimentary deposits can generally be divided into two categories in accordance with their predominant source of origin, either as "lithogenic" or "anthropogenic", or simply referred as "geochemical" and "man-made", respectively (9). Metals such as Zr, Rb and Sr which are derived from rock material by natural weathering processes, constitute the first group. The second group is made up of metals which have become enriched chiefly as a result of human activities and includes among others Cr, Co, Zn, Cd, Hg, and Pb.

Between these two groups there are combinations; for example, the enrichment of mobile elements such as Fe, which may well have had civilizational origins. By their own accumulation, these metals can cause other elements to accumulate (9).

Considering the values given in Table 2 and comparing the concentration of some trace metals in different geological formations, it is obvious that sediments from Abu-Simble and Arkin have relatively high content of trace metals. This elevated metal content in Abu-Simble could be a consequence of the increased population and industry in this city.

The influence of irrigation return drainage, as the water is used for extensive agricultural development, and the discharges from small industries may be also an explanation. Similar to Abu-Simble, Arkin is the first station next to Wady Halfa, which is a trade center and relatively populated.

Finally, it might be concluded that the area of Naser lake could be used as a pre-industrialized area and proposed as a suitable site for continuous and systematic monitoring.

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LOW INPUT CONCEPT FOR DESERT AGRICULTURE.

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1. Introduction: Population and food demand.

United Nations projections show that the world population has doubled during the last four decades to reach currently more than 5000 millions. Further expansion to more than 6000 millions by the year 2000 and 10000 millions later in the next century is expected (United Nations 1989). More than 90% of this increase is occurring in developing countries. The increase in population together with the anticipated social improvements will cause the demand for food to expand at an annual rate of more than 3%.

In contrast to the expansion of population and food demand the cultivated area per capita is decreasing with a mean decline rate of -33% in twenty years from 1964 to 1984 (table 1). The lowest decline rates occurred in the Americas and Europe while the highest are observed in the Middle East and Africa, where the decrease of agricultural land per capita reaches dramatic dimensions of more than 50%. This decrease reflects in first place the population development in addition to the loss of agricultural land related directly or indirectly to the population increase.

The loss of cropland is a matter of serious concern. Unfortunately, there is no reliable data to evaluate this drama of man destroying the basis of his own existence. According to estimates of Wollman and Fornier (1987), however, about 4% of all potentially productive agricultural land and about 25% of all highly productive land may be lost by the year 2000.

The loss of agricultural land may be divided into two distinct categories:

1. Loss of land due to the shift in priorities of land utilization (often related to population pres sures) permitting the use of productive land for building roads, industrial projects or urban facilities, and
2. destruction of agricultural land through mismanagement.

Well known forms of agricultural mismanagement which may destroy the soil is the misuse of water and fertilizers. This is especially valid for desert agriculture.

Table 1: Decline of cultivated area per capita during 20 years.

Region	Cultivated area, ha per capita		Relative decline, %
	1964	1984	
World	0.44	0.33	-33
America, South	0.49	0.45	- 8
America, North	1.05	0.90	-14
Western Europe	0.31	0.25	-19
Far East	0.30	0.20	-33
Middle East	0.53	0.35	-34
Africa	0.74	0.35	-53

World Commission 1987.

2. Desert agriculture: Between ecological and socioeconomic pressures.

The development of arid lands has been driven mainly by the need to provide food for the dramatically increasing population. Desert agriculture means therefore food production not only under the specific stress of the desert environment but also under the socioeconomic constraints of the growing population. Under these conditions intensive land utilization strategies originally developed to function under much more favourable conditions are often adopted. Many high input technologies are indeed politically very attractive. These include modern high yielding crop varieties with high demand for fertilizers, water and plant protection. The transfer of these technologies to the desert tries to fit the system to meet these requirement and often ignores or oversees the limited capacity of the system predestinated by climate and soil characteristics. Due to the lack of knowledge about the functioning of desert systems ecological consequences and sustainability of the system are often not taken into account. The result is an irreversible damage to the project to add a further case of "loss of agricultural land".

3. Low input concept

Many research activities in the tropics and subtropics are now directed to the development of low input agricultural techniques (Sanches and Salinas 1981, Kidd and Pimentel 1992). The low input concept does not aim at eliminating fertilizers, water and other essential inputs but reducing the requirements for these inputs to achieve reasonable, not necessarily maximal yields, through a series of practices based on a detailed knowledge of the system. Most important examples of these practices are:

1. Use of crop species and varieties that are more tolerant to drought, salinity and low fertility constraints.
2. Give priority to crops suited to water saving, efficient irrigation systems (drip irrigation in comparison to sprinkling).
3. Maximize nutrient use efficiency by:
   a) improving the retention of nutrients and enhancing the humus content through the application of green manures,
   b) adjusting the application of water and nutrients to the requirements of the crop during its development,
   c) identifying and quantifying nutrient losses through leaching and volatilization.
4. Maximize the use of biological nitrogen fixation and other symbiotic (mykorrhizal) systems.
5. To evaluate the use of mixed cropping systems with deep rooting multipurpose trees to improve water and nutrient efficiency (for example Leucaena leucocephala).
6. Monitor water quality and the development of salt status in the soil in order to try to adjust a tolerable salt cycle in the system, and to evaluate the need and possibility for salt leaching.
7 Never to apply any additives to desert soils before evaluating the consequences for water and salt relations of the system. Examples of such additives are clay and industrial "soil conditioners".

Some few aspects related to these measures are briefly discussed.

4. Soils under arid conditions.

Under the action of physical, chemical and biological weathering, parent geological materials are transformed into soils with time. Soils are therefor a product of not only the parent rock but also of their environment (Fuller 1974).

Water plays a significant role in weathering and soil formation: as a medium for all related chemical and biological transformations and all translocation processes. Desert soils are classed as "Aridisols", i.e. soils of the dry areas. Significant consequences of soil formation under arid conditions are low or almost absent humus content as well as salt accumulation. Soluble salts which are released in the course of weathering are not leached out. They may be translocated for some depth depending on rainfall to be precipitated when the soil dries out. Examples of typical precipitates are carbonates(lime) and sulphates (gypsum) of Ca, Mg and Na. Depending on the base content the pH tends to be alkaline, except in gypsum rich layers. Gravel and sand may predominate, however, in the top layer with low ion exchange capacity and low retention of water, nutrient and salt.

Egypt is a desert with several oases: one major Nile Basin Oasis and several smaller oases in the west. Geographically the desert of Egypt is often divided into three parts: the western desert, 670

* 10^3 km^2, extending from the Nile Valley westwards, the eastern desert, 225 * 10^3 km^2, between the Nile Valley and the Red Sea, and the Sinai Peninsula, 61 * 10^3 km^2 (Kassas 1991).

5. Water and salt relations.

According to precipitation, however, Egypt may be divided into 3 Zones with precipitation decreasing southwards:

1. the coastal area along the Mediterranean shore with annual rainfall from 100 to 150 mm,
2. a middle belt between the latitudes 31°N and 30 °N with annual rainfall ranging from 25 to 100 mm, and
3. the extremely arid area south of latitude 30 °N.

For example, Cairo is located at latitude 30 °N with a mean winter rainfall of about 27 mm. Figure 1 shows the frequency distribution of annual rainfall near Cairo indicating considerable variation. In addition the annual rate may be precipitated within a short time to leave the rest of the year dry with a considerable evapotranspiration potential. This indicates that plant production will be possible only through irrigation. Under these conditions, the plant characteristics related to transpiration and the irrigation technique will be of special significance for the water use efficiency of the system.

A consequence of a coarse textured top soil is the rapid water movement to deeper layers, A favourable effect of this is a reduction of evaporation and related salt accumulation in the top layer. Depending on the history of the site and conditions of wind and water erosion as well as related removal or deposition of fine material some layers may include silt and clay components which

Table 2: Soil water content (% wt.) in the desert east to Cairo as dependent on rainfall and soil depth.

Rainfall							
Date	7. Feb.	10. Feb.	13. May	23. Nov.	19. Dec.	26. Jan.	17. Mar.
mm	2.9	0.4	0.2	6.1	6.9	9.6	9.2
Soil water							
Date	17. Feb.	7. Apr.	23. Jun.	19. Sept.	22. Dec.	17. Mar.	8. Jun.
Depth, cm							
5	2.7	0.6	0.3	0.4	2.7	2.8	0.3
10	2.0	1.1	0.3	0.7	4.3	3.3	0.4
25	1.0	1.6	1.0	0.8	1.2	2.5	1.3
50	3.2	3.3	3.2	2.6	2.7	6.0	5.2
75	2.9	2.7	2.8	3.5	3.4	2.7	4.0

Walter and Breckle 1984.

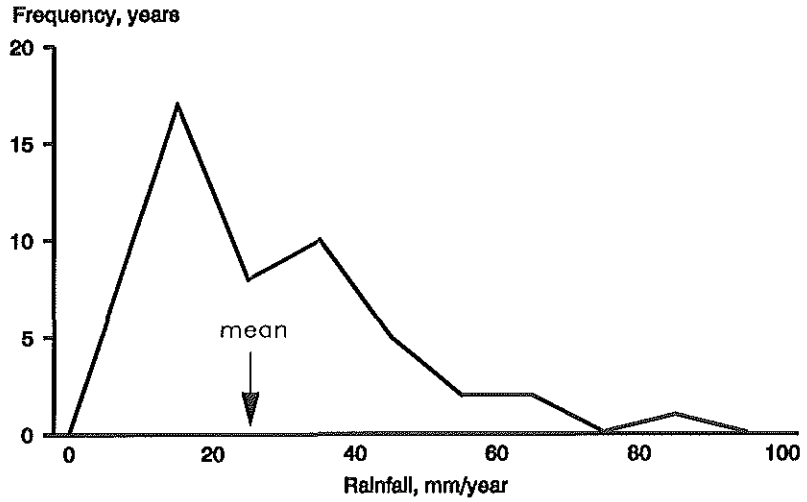

Figure 1: Frequency distribution of annual rainfall near Cairo during the period 1906-1950. (Walter and Breckle 1984).

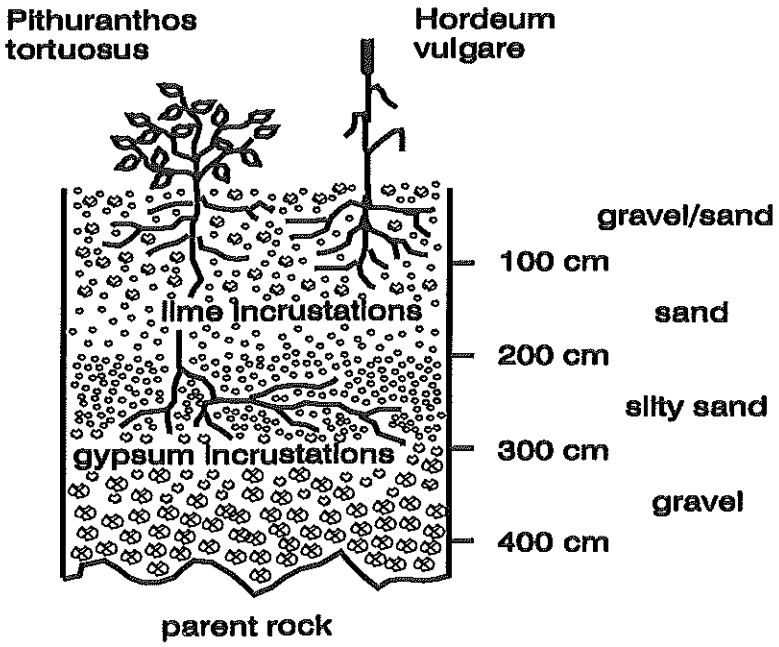

Figure 2: Soil profile with contrasting root systems of Pituranthos tortuosus and Hordeum vulgare of a Wadi near Cairo-Suez high way.

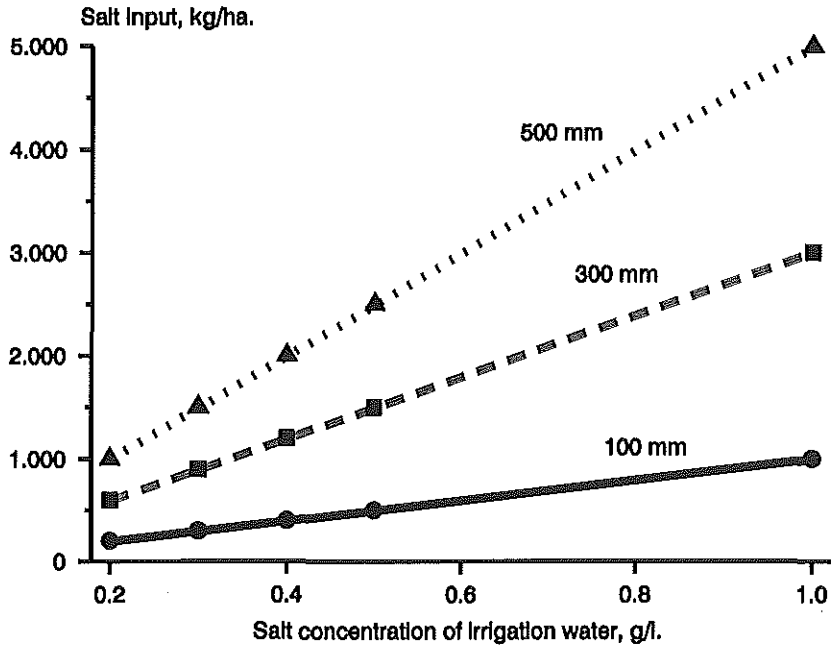

Figure 3: Salt input (kg/ha) with irrigation water depending on water quality and irrigation rate.

improve the water holding capacity of the layer. Such layers may retain water even during rain less periods when the top layers dries out (table 2). It is therefore evident that the deep rooting may be a significant aspect of water use efficiency (figure 2). Furthermore all measures and soil additives which improve water retention in the top layer of arid soils may increase evaporation loss, reduce water use efficiency and enhance salt accumulation.

Salt input with irrigation water under arid conditions is a matter of serious concern. As indicated in figure 3 several tons of salt per hectare may be introduced into soil annually with the irrigation water. This fact must be fully accounted for in any irrigated project under arid conditions. The sustainability of the system will be determined by the question about the fate of this salt. A salt balance is therefor a must for evaluating the adequacy of the irrigation technique, for the choice of crops and cropping systems and for estimating the leaching requirement. Fortunately, there is considerable potential for improving both water use efficiency and salt tolerance of crops (Helal 1983).

6. Nutrient relations of soils and crops.

In natural ecosystems plant nutrients are transferred between soil and plant in more or less closed cycles with both nutrient fluxes (from soil to plant and from plant to soil) adjusted to the cycling

capacity of the system. Agricultural practices disturb this cycle in several ways the most obvious of which are the nutrient inputs as fertilizers nutrient removal with the harvest , and the lack of adjustment of both to each other. The ratio of nutrient removal with the harvest to nutrient input as fertilizer, i.e. the nutrient recovery is a measure for the nutrient efficiency of the plant-soil system under prevailing conditions. The efficiency of fertilizer utilization depends on the uptake and metabolism of nutrients (figure 4). Nutrient efficiency of crops is generally low under all climatic conditions with some quantitative differences (table 4, 5). N-recovery levels of 50% are normal under temperature conditions. Under ecological stresses of the arid region the utilization of nutrients may be even much lower (Craswell and Godwin 1984).

A significant component of low input principles is to maximize fertilizer utilization. For the development of concepts and measures to achieve this, an understanding of related soil and plant characteristics and processes is essential.

During the last decades, considerable progress has been achieved towards clarifying soil and plant factors related to the uptake of nutrients by growing plants (Barber 1984, Pitman 1972, Helal 1992). Most important parameters listed in table 3 may be divided into four categories according to their mode of action:

1. Nutrient availability in soils (1-4).
2. Acquisition of nutrients by growing roots (5-8).
3. Nutrient retention and nutrient loss (9).
4. Effect of plant growth (10).

The parameters listed in table 3 indicate that water availability may affect nutrient uptake and utilization in various ways, namely by modifying all categories of related processes: availability, acquisition, retention and metabolic utilization of the nutrients.

Considering the genetic dependence of plant parameters related to nutrient efficiency (Randall et al. 1993), table 3 demonstrate a considerable potential for improving nutrient efficiency of crops.

The low efficiency of mineral nitrogen fertilizers in arid agriculture indicate, however, the need for nitrogen fixing systems. In multiple cropping systems nitrogen fertilizer inputs can be reduced or even entirely eliminated by including a nitrogen fixing species (Hargrove 1988). Multiple cropping systems use two or more different crops on the same area during a year in sequential or intercropping. Several nitrogen fixing species are available for low input multiple cropping systems ranging from conventional legume crops to perennial shrubs and trees, such as Leucaena leucocephala (Prinsley and Swift 1986). The species of choice will be determined not only by its nitrogen fixing efficiency but also by its water demand, salt tolerance and its contribution to the nutrient efficiency of the whole system.

Table 3: Soil and plant parameters related to nutrient uptake.

1	Nutrient concentration of soil solution.
2	Soil buffering capacity (retarding soil solution depletion).
3	Effective nutrient diffusion coefficient.
4	Transpiration rate (nutrient supply by convective flow).
5	Total root length and root growth rate.
6	Root distribution in soil profile.
7	Physiologically active part of the root.
8	Physiological root characteristics: maximal influx rate, nutrient affinity of the transport system.
9	Efflux rate: back leakage of nutrients.
10	Nutrient demand of the plant: proportional to growth rate.

$$(1)\quad \text{Agronomic efficiency} = \frac{\text{grain yield}_F - \text{grain yield}_C}{\text{fertilizer N applied}} \quad \text{kg/kg}$$

$$(2)\quad \text{Apparent nitrogen recovery} = \frac{\text{N uptake}_F - \text{N uptake}_C}{\text{fertilizer N applied}} \quad \text{kg/kg}$$

$$(3)\quad \text{Physiological efficiency} = \frac{\text{grain yield}_F - \text{grain yield}_C}{\text{N uptake}_F - \text{N uptake}_C} \quad \text{kg/kg}$$

F = fertilized crop, C = unfertilized control.

Figure 4: Nitrogen fertilizer efficiency.

Table 4: Nitrogen fertilizer efficiency for wheat and barley in regions with a mediterranean climate.

Location	Crop type	Maximum grain yield (ton/ha)	Agronomic efficiency (kg/kg)	Apparent recovery (%)	Physiological efficiency (kg/kg)
Australia	Spring wheat	3.0	6 - 16	28 - 50	22 - 32
Cyprus	Durum wheat	1.4	2 - 5	27 - 40	6 - 13
	Spring wheat	2.1	0 - 11	14 -43	1 - 25
	Barley	1.8	1 - 4	15 - 32	7 - 13
Turkey	Spring wheat	5.1	11 - 28	27 - 67	30 - 57
Morocco	Spring wheat	2.3	3	26	11
Italy	Spring wheat	4.6	5 - 24	21 - 71	14 - 79
Greece	Spring wheat	3.3	0 - 5	14 - 40	3 - 24
Lebanon	Spring wheat	7.9	12 - 24	20 - 67	44 - 72
Egypt	Spring wheat	5.9	1 - 22	28 - 62	2 - 65
Iran	Spring wheat	5.2	4 - 19	14 - 60	16 - 32

Craswell and Godwin 1984

Table 5: Nitrogen fertilizer efficiency for Sorghum and wheat in the semiarid tropics.

Location	Crop type	Maximum grain yield (ton/ha)	Agronomic efficiency (kg/kg)	Apparent recovery (%)	Physiological efficiency (kg/kg)
Katherine (Australia)	Grain sorghum	4.3	7 - 22	28 - 61	22 - 46
Katherine (Australia)	Grain sorghum	5.4	2 - 13	1 - 35	15 - 190
Delhi (India)	Grain sorghum	5.4	14 - 24	48 -84	28 - 39
Gezira (Sudan)	Irrigated spring wheat	1.8	3 - 8	21 - 36	13 - 23
Lyallpur (Pakistan)	Spring wheat	4.5	12 - 23	44 - 68	23 - 37
Tandojam (Pakistan)	Spring wheat	2.2	2 - 9	14 - 37	15 - 26
India	Spring wheat	5.4	4 - 29	18 - 77	19 - 77
Pakistan	Spring wheat	5.7	0 - 32	6 - 89	0 - 42

Craswell and Godwin 1984

7. The Inshas Project: Water and fertilizers in desert agriculture.

To carry out and evaluate various aspects of low input strategy in desert agriculture, the agricultural working group of Inshas Research Centre (Atomic Energy Authority of Egypt) was divided into four subgroups with the following objectives:

1. Cropping Systems:

a) Choice and selection of crop species and cultivars including nitrogen fixing systems with special consideration to their adaptation to drought and salt stress and to low nutrient supply.
b) Evaluation of plant growth, root development and crop yield under the conditions of the site.
c) Estimation of water and fertilizer requirements in co-operation with other groups.

2. Water and Salt:

a) Collection and registration of meteorological data and their use for evaluation of water and salt relations of the system.
b) Quantifying water and salt relations with various irrigation and cropping systems.
c) Working out irrigation limits considering the salt cycle and leaching requirements of the system.

3. Soils and Fertilizers:

a) Determination of soil physical, chemical and biological parameters related to water, salt and nutrient relations and carrying out all related water and soil analyses.
b) Establishing and evaluating of symbiotic systems.
c) Evaluating of nutrient efficiency with various irrigation and cropping systems.

4. Animal Production:

a) Choice of animals adapted to arid conditions.
b) Evaluation of the fodder quality produced under conditions of the site.
c) Determination of the contribution of the animals to the salt and nutrient cycles of the system.

Acknowledgement

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LYSIMETER AND GREENHOUSE STUDY USING NITROGEN- 15 ON N-LOSSES AND N-UPTAKE BY WHEAT AND CORN AS AFFECTED BY SOIL CONDITIONER AND NITRIFICATION INHIBITOR.

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ABSTRACT

Due to its poor physical and chemical properties, cultivation of the newely reclaimed sandy soil needs not only application of nutrients but also keeping them from losses. In lysimeter experiment, the effect of polyacrylamide (PAM) as soil conditioner and dicyandiamide (DCD) as nitrification inhibitor on nitrogen losses and N-uptaken by wheat was studied. N-15 labelled urea(2% atom ex.) was applied at the rate of 100 kg N/acre without or with PAM and/or DCD. Plants were harvested at full maturity,dry matter was recorded and N-uptaken, Ndff, and N-losses were calculated. In separate greenhouse experiment , pots filled with 10 kg soil were planted with corn and treated with labelled urea without or with DCD at a rate of 120 kg N/acre,plants were harvested after 60 days.Results indicate that both PAM and DCD have significant effect on increasing the straw and grain yield of the wheat. Nitrogen recovery by whole wheat plant increased from 27.8 % when urea was applied alone to 61.1 % for urea + PAM + DCD. At the same time N-losses decrease from 63.4 % to 23.4 % . Both dry matter yield and N-uptake by corn increased significantly due to DCD addition, and losses of nitrogen decreased from 52.4 % to 24.9 % . Use of PAM and DCD could have positive impact on crop production in the sandy soil.

INTRODUCTION

Cultivation of new sandy areas in Egypt became a necessity to increase agricultural production in order to face the fast growing population . These soils are generally poor in respect to physical properties, mineral and organic colloids and nutrient supply. Although fertilization of sandy soils is a necessary practice, nutrients are subject to loss by irrigation water.

One possibility to increase yields in these soils is by using soil conditioners. De Boodt(1979) reported that , the main objects of using soil conditioners are : promoting germination , improving drainge, combating water erosin, and reducing evaporation from the soil surface under arid conditions.,

Polymers and related products variously proposed for soil conditioning can be classified to non-ionized polyanions,polycations strong dipole polymers and bitumen emulsions (De Boodt , 1972). Several researchers have showen the effectiveness of polyacrylamide (PAM) in improving the physical properties of the sandy soils(Vandevelde and De Boodt,(1972),Hartmann et-al.(1976),and Salem(1987).

Due to its light texture,sandy soils losses the applied nitrogen fertilizers as nitrate leached with the irrigation water . Ideally,with the conservation of NH4, or urea-N to NO3 inhibited, losses associated with leaching can be controlled and economic and environmental benefits will occur. Dicyandiamide (DCD) was found not to be only effective in reducing nitrogen losses(Amberger,1989, Abdel Sabour and Abdel Monem,1991)but also,its application resulted in increase in crop yield. Frye et.al.(1989) reported that, on the sandy soil of Florida, corn grain yield responded significantly to application of DCD with urea . DCD increased grain yield by 29% and 40 % ,as compared to urea without DCD.

In this study, a lysimeter experiment was conducted to evaluate the effect of nitrogen fertilization applied as N-15 labelled urea on wheat yield and N-uptake,as well as N-losses, from applied urea as affected by application of polyacrylamide solution (PAM) as soil conditioner , and Dicyandiamide (DCD) as nitrification inhibitor. Another greenhouse experiment was carried out to evaluate the effect of DCD,when added with urea,on the dry matter yield of the shoots and roots of corn , as well as N-uptake and nitrogen losses from the applied labelled urea.

MATERIAL AND METHODS:

The effect of soil conditioner (PAM),and nitrification inhibitor (DCD) on yield and N-uptake by wheat grown in sandy soil was studied in lysimeter experiment . Lysimeters (60cm ID ,100 cm hight) were filled with sandy soils collected from Inshas area with 93 % sand,4.5% silt and 2.5% clay , orgacic matter content is 0.1 % and PH (1:2.5 Kcl) is 7.6. Lysimter were placed in randomized block design with four replications. Constant treatments (9gram P as superphosphate,7.5 gram K as potassium sulphate and 3.75/gram Mg as magnsium sulphate) were uniformaly mixed. Wheat seeds (triticum aestivmm,cv. sakha 92)were planted at rate of 19 seeds/lysimeter. Nitrogen fertilizers were applied at rate of 100 / Kg N/acre urea enriched with 2 atoms % N-15 was applied alone in the control treatment, labelled urea + 2 % PAM, labelled urea + 0.2 % PAM (mixed with the soil surface) ,and labelled urea + 2% DCD + 0.2% PAM were the four treatments used in this study . Nitrogen

fertilizers were applied as third at tellering,and two thirds at shooting stage.Plants were harvested after 17 weeks,at full maturity.The aboveground portion were then separated into grains and straw,and the dry weight was recorded. The oven dried (70°C) plant materials were ground and prepared for N-15 analysis.Sample preparation and isotope analysis were determined according to Faust (1980).

Greenhouse experiment with corn(Zea mays L.) was carried out in plastic pots containing 10 Kg of the same sandy soil used in the lysimeter experiment. One level of nitrogen was used(120 Kg N/acre) was applied as N-15 labelled urea,or as labelled urea + 2 % DCD. Three replications were used in this experiment. All pots recevied a basel dressing of 20 KgP2 O5/acre as superphosphate and 25 Kg K2O/acre as potassium sulphate,uniformly mixed with the soil . The nitrogen fertilizer was added as solution in two doses after 7 and 17 days of germination. Five seeds of corn were planted , after germination , the seedlings were thinned to only three per pot . Plants were harvested after 60 days, dried at 70° C, ground and prepared for N-15 analysis.

RESULTS AND DISCUSSION

The impact of the soil conditioner (PAM),and the nitrification inhibitor (DCD) on straw and grain yield is shown in table (1). Data revealed that application of PAM and DCD in addition to the urea firtilizer ,increased the straw and grain yield , 30.6 % and 39.6 % respectivily. The incease in yield according to the treatment decreased in the following order ,Urea + PAM + DCD / Urea + DCD / Urea + PAM / Urea.

The significant increase in the dry matter yield when soil was treated with PAM and DCD may due to the combined effect of the two materials. The effect of PAM may partially be due to the hydrophillicity of the material(Hardmann et.al. 1976),giving better destribution of the water and nutrient solution. Another reason may be the presance of N in the PAM molucle ($-CONH_2$) (Kachinsky and Moso Lova,1976). On the other hand,the effect of DCD on the dry matter yield in the presance of PAM may due to its role in reducing N-losses (Amberger,1989), in addition to the fact that DCD completly

decomposes in the soil to CO_2 and NH_4 over several weeks and therby acts as a high analysis (66.7 %) slow release fertilizer .

It is worthmentioning that, application of PAM to the sandy soil fertilized with urea , increased the dry matter yield of the whole plant by 5.5 % . Simillar results were obtained by Salem(1987). Growth response of crops depends on the nature of the soil conditioner and the soil type (Salem, 1987). (Gad, 1984) reported that PAM was more favourable with alluvial soils than with sandy soils. Afifi et.al. (1990) reported that conditioning the sandy soil with PAM slightly increased the yield of wheat.

Regarding the N-uptake by wheat as affected by urea alone or with DCD and PAM,data presented in table (1) showed significant increase in shoot N-uptake as well as grain N-uptake due to fertilization with Urea + PAM + DCD as compared to application of Urea. The percentage increase in N-uptake were 38.8 and 35.9% for wheat shoot and grain respectively. Increase in nitrogen uptake in grain would have positive effect on the nutrait value of the wheat, used as bread. Application of DCD with urea did not effect the N-uptake by wheat . Although N-uptake in straw or grain tended to increase as DCD was applied, this increase is not significant. Katyal et.al. (1987) reported that addition of DCD to urea did not seem to effect the apparent recovery by wheat. Amberger and Bauer (1990),explained that soil type had a strong effect on performance of the inhibitor, in addition,they reported that DCD did not show any effect after 5 weeks.

Nitrogen fertilizer uptake efficiency has been defined by real utilization coefficient (RUC) (Remy and Viaux,1982). RUC could be obtained as follow:

$$RUC = \frac{Un * e}{F * e_o}$$

Where Un is the N-uptake , and e is the isotopic excess in the plant at harvest, F is the amount of fertilizer N applied and eo its isotopic excess.

Data from table (1) revealed that RUC ranged from 32% to 51% according to the treatment. Application of the soil conditioner or / and nitrification inhibitor increased the nitrogen fertilizer uptake efficiency . Machet et.al. (1987) reported that RUC generally held to be in the range 20-80 % at harvest,they reported that the variablety arising from the interaction between factors such as form the fertilizer, type of soil and climatic conditions. Lower RUC for urea treatment could be attributed to N-losses and poor chemical and physical properties of the sand soil .

The contribution of fertilizer N to the total N content of shoot and grain as well as in soil is presented in table (2).The proportion of nitrogen derived from fertilizer (Ndff) in grain averaged 692.5 mg N/lysimeter,while Ndff in shoot average 162.5 mg N/Lys. The proporation of nitrogen derived from the applied urea in grain or shoot was more than doubled when wheat was fertilized with urea +PAM +DCD as compared with fertilization with urea alone. Also Ndff in both plant parts was increased by application of urea + PAM and urea + DCD but in less degree than urea + PAM + DCD . Effect of PAM on Ndff may due to its effect on the dry matter content. Metwally et.al (1992) reported increase ranged from 6.8 % to 40.6 % in dry matter yield of wheat planted in sandy soil and treated with PAM . As was reported by Malzer et.al. (1989) , the crop benefits associated with the inhibition of nitrification are most frequently related to the indirect benfit of reduceing fertilizer N-losses through leaching or denitrification. Soliman and Abdel Monem (1992) reported significant increase in Ndff in whole plant of wheat grown in sandy soil as treated with urea + DCD,when compared with fertilization with urea.

Data of table (3) show that , dry matter of the corn was significantly increased by the application of urea + DCD as compared with urea alone , which was also reflected on N-uptake . Although Malzer et.al(1989) reported increase of 23% of corn yield as affect by DCD application in sandy soil, results of table (3), indicated that 34% of corn dry matter was increased due to fertilization with urea + DCD, as compared with urea . Malzer et. al. (1989) explained that magnitude of yield increase due to nitrification inhibitor depends on soil type, time, of N application and environmental conditions. As real utilization coefficient (RUC) was calculated

its values presented in table (3) show increase from 28 to 61 % due to applic-ation of DCD,which reflected better uptake efficiency by plant when fertilized with urea + DCD. Also Ndff was increased significantly in plant when DCD was added,as indicated in table(3).

Fig. (1) presentes the percentage of N-recovered by plant and soil, as well as N-losses for wheat and corn treated with N-15 labelled urea and labelled urea + DCD. Data show that more than half (52 %) of the applied -N as urea to corn was lost, while, this percentage increase to 64 % in the case of wheat. This high percentage of losses may due to mainly to the soil texture (sandy soil), Abdel Monem (1986) and Abdel Monem and Ryan (1991) reported losses of less than 20 % of the applied urea to wheat in clay soil, while Soliman et.al (1992) found that 49 % of the applied labelled urea to the sandy soil was lost through leaching, as well as volatilization. Abdel Monem et.al. (1990) explained that low losses in clay soils as compared to the sandy soils may due to the high cation exchange capacity (CEC) of the clay soils, which prevent NH_4 to be lost . Similar results were obtained by Katyal and Gadalla (1989).

Addition of DCD to urea decreased the N-losses for the both crops, from 64 % to 24 % ,and from 52% to 25% for wheat and corn respecively . The crop benefits associated with the inhibition of nitrification are most frequently related to indirect benefit of reducing fertilizer N-loss through leaching or volatilization.

Table (1) wheat yield,nitrogen uptake and real uitilization coefficient (RUC) as affected by fertilizer application.

Treatment	Dry matter g/Lys		N-uptake mg/Lys.		RUC
	shoot	Grain	Shoot	Grain	
Urea	137.6	60.0	619.1	1062.0	32
Urea + PAM	148.4	71.3	771.1	1204.5	39
Urea + DCD	154.2	73.0	755.6	1292.6	45
Urea + PAM + DCD	186.2	88.2	856.7	1442.9	51
LSD 0.05	19.7	11.6	186.7	233.6	

Table (2) Nitrogen drived from fertilizer (Ndff) in wheat plant and soil as affected by Urea and Urea + DCD

Treatment	Ndff (mg/Lysimetet)			
	Shoot	Grain	Soil	Total
Urea	103.7	433.4	169.1	706.2
Urea + PAM	146.7	626.7	204.9	978.3
Urea + DCD	184.9	743.0	331.6	1259.5
Urea + PAM + DCD	214.5	965.5	296.3	1476.3

Table (3) Corn dry matter, N-uptake, nitrogen dervied from fertilizer (Ndff) in corn plant and soil and RUC as affected by urea and urea + DCD.

Treatment	Dry matter	N-uptake	RUC	Ndff (mg/pot)		
	9/pot	mg/pot		plant	soil	total
Urea	36.6	1116.0	27.5	330.3	241.0	571.3
Urea + DCD	48.9	1476.8	61.6	738.0	409.3	1147.3
LSD 0.05	7.5	234.9				

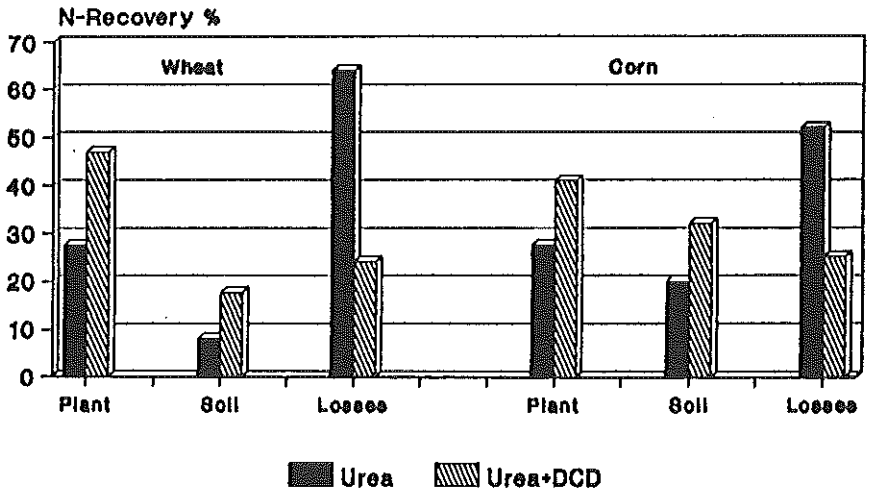

Fig (1) Perentage of N-recavered by plant and soil and losses as affected by urea and urea + DCD.

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BENEFITS OF ORGANIC MATTER (HUMUS) IN ARID IRRIGATED SOILS

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General characteristics of dryland soils and agriculture

Arid and semiarid regions comprise almost 40 % of the worlds land area and are inhabited by about 700 million people with growing tendencies. Many of these dryland areas are typified by a highly fragile natural resource base. Soils are often coarse textured, sandy and low in inherent fertility. They generally contain little organic matter and therefore, have a low water-holding capacity. With respect to the growing population and their demand for food and fiber, it is an important goal to develop on newly reclaimed irrigated land in the arid region a sustainable farming system. This means to develop systems that are productive and profitable, to enhance economic soil and irrigation water conservation practices, to protect nutrients from losses, and do so over the long-term. It furthermore, emphasizes such cultural practices as crop rotations, recycling of animal manures, control of soil erosion and to maintain or enhance soil productivity.

SUSTAINABLE AGRICULTURE

That is an Agriculture With

Low-Input Methods and Skilled Management and Uses Among Others

Reduced Synthetic Chemical Inputs	Crop rotations	Crop-Livestock Diversifications
Soil and Water Conservation Practices	Use of Animal and Green Manures, and Organic Wastes	

Beside the restricted availability of good and sufficient irrigation water, the most serious drawback in the developement of new farming systems in arid and semiarid areas is a lack of soil organic matter, and the difficulties in establishing and maintaining it on sufficient and stable levels. Even relative small levels, however, have great benefits compared to purely mineral soils (table 1).

Table 1: Beneficial properties of humus in fostering fertility of sandy arid soils

Properties	Remarks	Effects on Soil
Water retention	Organic matter holds up to 20 times its weight in water	Improves water-holding capacity substantially in sandy soils. Prevents drying and shrinking
Store of nutrients	Mineralization yields CO_2, N, P, S, and other mineral nutrients	Slow release fertilizer and saves frequent and costly supply
Chelation	Forms complexes with Cu^{2+}, Mn^{2+}, Zn^{2+} and others	Enhances availability of micronutrients to plants
Soil structure	Cements particles into structural units called aggregates	Improves structure, gas exchange, inhibits erosion
Buffer action	Buffers both acid and alkaline ranges	Maintains a more uniform reaction in soil

Humus can absorb great amounts of water and therefore, improves substantially the water holding capacity of mineral, and in particular of sandy soils. It increases the range of available water, since in sandy or gravelly soils the difference between field capacity and permanent wilting point is rather small. This has con-

siderable implications for the amount, frequency and methods of irrigation. In adition to this and other physical properties, humus is a slow release fertilizer for macro- and micronutrients. In the sandy soils the nitrogen use efficiency is very low and ranges only from 5 to 10 %. The loss of water through deep percolation in the sandy soils leads to nitrogen losses, and nitrate pollution of water bodies is one of the consequences. Phosphorus is sometimes added in great amounts because of the presence of calcium carbonate and no consideration is taken of the residual effects of phosphatic fertilizer, which particular in presence of some humic reserves may be applied in smaller amounts for two or three progressive growing seasons.

The relatively high levels of calcium carbonate also restrict the availability of nutrients such as potassium, magnesium, iron and zinc. Complexation of these mineral nutrients by humus molecules provides a much better supply to plants.

It also improves soil structure by forming organo-mineral complexes and aggregates which leads to a better porosity, gas exchange and inhibits erosion. Humus also inhibits acidification or alkalinization of soils and therefore, maintains a more uniform reaction in soil.

The specificities of Egypt dictate to optimize the economic use of water and other natural resources

With respect to the rapidly growing population, a limited base of old irrigated land and water supply, the governmental five years investment plan for land reclamation and the development of agriculture in Egypt stated in 1984, as a basic goal to "**fully exploit the available water supply, to provide more space for living and to maximize the food production potential of the country**"

According to table 2, the present agricultural land in Egypt occupies about 2.5 million hectars or 5.8 million feddans. This amounts only to 3 % of the country's total surface area and is mostly confined to the immediate margins of the Nile River and the Nile Delta on the Mediterranean coast. Agriculture in Egypt still accounts for 40 % of total employment and is, therefore, the largest sector of the Egyptian economy. Arable land per capita, however, is declining and corresponded in 1984 to 0.05 ha. Average farm size is declining likewise and 95 % of the holdings were in 1983 in the size of less than 5 feddans or 2.1 ha (Kishk and Bailey, 1988).

Table 2: Available irrigated land at Egypt, population, and average size of farm holdings

Present size of irrigated land:	2.5 to 2.9 * 10^6 hectar ≡ 6 to 6.9 * 10^6 Feddans; ≈ 3 % of total area
Average farm sizes:	In 1969 38 % less than 5 Feddans In 1975 66 % " " " In 1983 95 % " " "
Population:	1989 ≈ 50 million year 2000 ≈ 70 - 80 million
Arable land per capita:	≈ 0.05 - 0.06 hectar
Additional irrigated land since 1813 until now:	900.000 hectar ≈ 2.2 * 10^6 Feddans
1952 to 1988:	600.000 hectar ≈ 1.5 * 10^6 Feddans

Despite of intensive cropping of two to three times a year and yields far above world averages of crops in irrigated land, the limited land base places severe limits on the growth of agricultural output. This increased during the 1970 for about 2 %, the population increase and the higher living standard has pushed, however, domestic food demand beyond the current supply capacity of

Egyptian agriculture, leading to a sharp increase in food imports. Egypt already imports about 50 % of its food, and an further increase would burden its already strained economy (Starr, 1993).

For these reasons reclamtion of new land receives uttermost consideration and large-scale land reclamation has been carried on in Egypt for over one century. It began with efforts under the reign of Mohamed Ali in the northern delta, which brought between 1813 to 1852 some 600,000 feddans into production. Most of the land, however was reclaimed after revolution from 1952 on and corresponded until 1988 additional 600.000 hectar or 1.5 million feddan. The overall hyper-arid climate of almost Egypt, and the moisture deficit between evapotranspiration and precipitation by rain can only be covered by extensive irrigation of agricultural land. Although there is plenty of land resource for future agricultural expansion and there is a surplus of skilled farm labour available, the real problem is the limitation of available irrigation water (table 3).

Table 3: Annual water budget (El-Kholi and El Gindy, 1991; Starr, 1993)

Annual resources 10^9 m^3		**Annual Consumption 10^9 m^3**	
Nile downstream discharge	55.5	Irrigation of old cultivated area	48
Ground water	0.5	Industrial and domestic use	1
		Irrig. of reclaimed area	4
		Discharge to sea	3
Sum	**56**		**56**

According to data, kindly provided by Dr. El-Kholi (1991) and by Joyce Starr (1993), the total annually available water resources of 56 * 10^9 m^3 (55.5 Nile river downstream discharge and 0.5 groundwater) are completely consumed in irrigation (old and newly reclaimed areas), domestic use and power. Presently used ground water is fed from big water reserves below the Sahara (Klitzsch, 1991). According to ^{14}C dating these reserves have been formed during wet seasons 11,000 to 3,500 BP. They are, however, not continuously renewed and have therefore, only a very limted availability to supply a continuous irrigation.

Of course water use-efficiency in most of the old agricultural area could be improved, since in the presently used surface irrigation practices, it only ranges to about 20 %. The deep water percolation furthermore, causes tremendous losses (Kishk and Bailey, 1988). For these reasons, more effective irrigation techniques in the newly reclaimed areas are prescribed. But in order to decrease water and fertilizer demands, and to generally improve soil fertility, a prospective care in establishing and maintaining a sufficient soil organic matter level is a necessity.

Virgin uncultivated and unreclaimed arid soils are exceptionally low in microbial numbers and activities. By adding organic residues and composts food and energy is provided to microorganisms in soil which are the driving force and the catalysts for most of the ongoing fortunate processes shown in Table 1. Even plant growth largely promotes microbial activity by incorporation of root and plant residues to soil, and by root deposits. In a wheat field of our humid area, about half of the photosynthesates, or more than 2000 kg of carbon per hectar, are transported downward and used

for root growth, root respiration and rhizodeposits (Swinnen, 1994).

Secondary Salinization

Active microbial live and moderate humus levels are also of great help in inhibiting or facilitating secondary salinization of irrigated soils. Due to the lack of precipitation and to the continuous supply of irrigation water with at least a low amount of soluble salts, these are accumulated with time in irrigated soils (Szabolcs, 1989; Helal and Issa, 1994 this volume). This well known effect is one of the biggest problems in irrigated areas and 20 - 30 % of these areas in the world are damaged by this effect and go out of production (Brown et. al. 1990). Even with good quality water and a sufficient drainage system, irrigation leads sooner or later to problems caused by secondary salinization. Furthermore, the hazard of raising the groundwater table has been underestimated because even when the water table has been 10 to 20 m below the surface before constructing the irrigation system, it can easily be elevated into the 1 to 2 m region below surface when drainage is poor. In 1900 when perennial irrigation started in Egypt, because of the changes in the salt and water regime, the Nile Delta became salinized and an artificial drainage system became necessary to eliminate excess salt.

Application of sulfur or gypsum to reclaim soils damaged by secondary salinization is certainly rather effective. These acidifying agents solubilize $CaCO_3$ and release Ca^{+2} ions, but even when available, they are costly and need labor - and mainly plenty of water for leaching and drainage of excess salts.

Presently biological methods through the addition of organic residues used in Pakistan and India, aim to speed up the biological activity in secondary salt affected soils.

Addition of decomposable green manure, residues of straw, rice husks or animal manure cause the release of CO_2 and lead to solubilization of Ca^{2+} by the reaction $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$. Exchange of Na^+ with Ca^{2+} on the exchange sites of the soil make this and other fixed detrimental ions soluble in water and they can be leached down. Exchange with Ca^{2+} also restored the soil structure and thus its permeability to water.

In many cases where fields are damaged by secondary salinization and went out of a profitable production of wheat or other crops, salt tolerant intermediate plants were grown and after some time they were used as green manure or partly for green fodder.

Table 4: Different species and varieties of salt tolerant plants, used in Pakistan as crops or for reclamation of land under secondary salinization (Malik et al. 1984).

Species	Root zone salinity associated with 50% green matter yield reduction (EC dS m^{-1})
Atriplex amnicola	33
Acacia cambagei	28
Leptochloa fusca (Kallar grass)	22
Brassica napus (Rape)	20
Beta vulgaris (Fodder Beet)	19
Hordeum vulgare (Barley varieties)	18-19
Sorghum vulgare (Millet varieties)	15-17
Sesbania spp. (N_2-fixing Legumes)	10-13

Several of these plants can even be irrigated with brackish water, and in addition are nitrogen fixing plants which then supply nitrogen to following crops.

Establishing these plants on area under secondary salinization, plant roots will increase the permeability of the subsoil. Excretion of CO_2 will reduce sodicity. The choice of plants is, however, restricted because they must be able to withstand salinity and even prolonged waterlogging in case of insufficient drainage. Natures treasury has supplied us with many species and varieties of plants which can be used for nutrition or fodder, or are applied as green manures for the improvement of soils heavily suffering from secondary salinization (table 4). Several of these plants like Sesbania spp. or Kallar grass, fix nitrogen and are therefore, supplying N-fertilizers to following crops. Particular the latter plant grows on highly saline sodic soil, can be irrigated with brackish water, and supplies domestic animals with fodder in areas which are not profitable for farming other crops.

Conclusions

Reclaiming of new land for agriculture is of high priority for the Egyptian economy. On the other hand the ecological conditions in this country are forcing to apply natural resources and mainly water as economically as possible. One of the measures to reach this goal is to establish and maintain a certain level of soil organic matter, which helps to increase the water holding capacity of soils and a much better and more economically use of costly fertilizers.

Nile silt and farmyard manures are the main traditional materials used in the reclaimed sandy soils to build up soil structure and for improving water and nutrient use efficiencies. They are get-

ting, however, too short in supply for being used on a bigger scale. Several projects have started already to test and evaluate the efficiency and economy of local materials of composts from city wastes. Although these materials are available in large amounts, and their use helps to solve problems of waste diposal, their application as a source for composts should be carefully checked for contaminants by toxic heavy metals and organic compounds. It also has been suggested to recycle water already used by the inhabitants of the big cities as a source for irrigation water. Again as said above for composts from city wastes, its suitability has to be controlled before application.

Prospects are now being more widely investigated in the application of salt-tolerant plants in the reclamation of land suffering by secondary salinization. Utilization of plants as shown in table 4 or selection of salt-tolerant species of wheat, cotton, sugar beets, rye grass, or oil and fodder crops should largely broaden the present base of traditional agriculture and allow even the use of saline and brackish waters.

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Lutz Christians

Environment - a Challenge for Architecture

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The last few decades saw a dramatic deterioration of environmental conditions. Nature has lost to a considerable degree her ability to regenerate from the effects of man-made contaminations, and we are harvesting in a very short time resources, which the earth took millions of years to build up.

In using these resources for our well-being, we damage the natural environment and thus cut the very branch, we are sitting on.

The awareness of this danger emerged just recently, about twenty years ago. It was Meadows' Report 1973 'The Limits of Growth' to the Club of Rome, which attracted world-wide attention to this problem. Like water from a burst dam, a flood of publications followed and has not stopped since. There is no week, that the media would not report on a new problem, of an environmental desaster, of a scandal or of political steps intended to be taken. We are beginning to live with the problem.

Not long ago, in 1979, the Technical University of Berlin celebrated its 100th anniversary. For that occasion, an impressive exhibition was mounted, which reminded us of the unconditional faith in technological progress prevailing in all strata of society one hundred years ago.

Today, we cannot imagine our life without the results of this progress - we just take it for granted. But, increasingly, we understand, that we will have to pay for it: Nature has begun to present the bill.

Konrad Lorenz, a Nobel-Prize winner and founder of the Comparative Behavoral Science once said: "Man is in progress, to eliminate himself. He is unable to recognize facts, when his genetic code ignores them. No inborn warning tells him, to protect his natural environment". With this Lorenz meant us, the 'Homo Faber' or the so-called civilized world.

We know, however, that people, whom we arrogantly called primitive, knew very well the limits of their fragile natural environment, when their very life depended on it. Meanwhile, we have learnt a little more and understand, why e. g. nomades can play a decisive role in maintaining semi-deserts for human habitat.

We read with respect of the wisdom of the Red Indians of North America in the 19th century. One Chief Seattle (1786 - 1866) said: "What befalls the Earth, will also befall us, the sons of the Earth. Man did not create the fabric of life - he is only a fibre in it. Whatever we do to this fabric, we do to ourselves".

It is sad to note, that people of this kind were usually on the losing side. Chico Mendes, a humble caoutchouc-collector in the Amazonas region, who became a prominent fighter against the destruction of the rain-forests, was simply shot dead by landowners, who wanted to expand their cattle-ranches. That happened in 1988.

It can be taken as good news, however, that Al Gore, shortly before his appointment as Vice-President of the USA, published 'Earth in Balance - Ecology and Human Spirit', which immediately became a bestseller worldwide. He writes "the modern industrial civilization collides violently with the eco-system of our planet. It is essential, to make preservation of our environment the focal point of our actions". In a comprehensive 'Marshall-Plan for the Earth' he then designs a strategy for the appli-

cation of birth-control, for the global preference of ecologically suitable technologies and for a general environmental education. "We can only succeed, when the majority recognizes the dangers and will act accordingly". This last statement is crucial, because we all will have to fight against ourselves and that is, as we know, the most difficult fight.

The problems, we are facing, are numerous and reach into all fields of our life. In many respects considerable progress has been made in the reduction of air-, water- and soil pollution and environmental technology has become a major growth sector with an annual turnover of 40 billion Marks. Some of these sectors have become a lucrative business already. Waste-disposal e. g. ranks very high and has proved very attractive, also for doubtful activities. Stricter controls and increasingly serious penalties for offenders are being introduced now.

The positive results in environmental research are accompanied by two problems:

The prevention or repair of environmental damages is costly. It is, therefore, legitimate, to expect the Industrialized Countries, who are also the main producers of pollution, to shoulder the higher part of the financial burden. But money alone will be no answer. What is required, is close and long-term cooperation in research and technological application between Industrialized and Developing Countries for mutual benefit. We must also learn, that ecological assessments of development projects are becoming inevitable. The ecological cost-benefit-analysis is no longer to be seen as a well-meant ethic request to protect nature, but as long-term economical consideration.

The Fraunhofer Institute published in 1992 a report, that the former West Germany accumulates an annual damage of

610 billion Marks to environment and health of people. In honest accountancy, this figure must be deducted from the GNP of 2760 billion Marks, i. e. more than 20%.

The other problem: There is no methodology, to bring together individual research-results into a comprehensive, interdependent system, such as nature is. Modern science is based on the principle, to break up complex systems into small, examinable units. The nature of this process requires and produces more and more specialization. There is an urgent need, however, to bring these units back into the complex puzzle, if an overall recovery of our environment is to be achieved.

What is now the role of architects and planners? Certainly, not only to comply with ever stricter regulations.

Good planning means a contribution to progress without causing harm to man and environment. This may stretch from far reaching decisions in regional planning to the choice of a material for interior decoration.

If a family decides to have an ecological home of the highest standard and selects for that purpose a site far out of town, it may result in daily travels with possibly two cars to and from town. The positive achievements of the eco-house are then neutralized via the exhaust-pipes.

The uncontrolled expansion of our cities, the urban sprawl, has created enormeous ecological problems. The tendency, to separate work and leisure, was supported by modern planning ideas (Le Corbusier and the Charter of Athens) and was only possible with modern means of transport, especially the private motor-car. As long as fuel is cheaply available and the political support for the construction of small family-houses continues, there will be no solution to the environmental crisis.

Vehicular traffic as result of settlement-planning is difficult to predict, but measurable after completion. The well-known Austrian architect Roland Rainer observed, that inhabitants of the Puchenau-colony near Linz, which he had designed, preferred to stay at home over weekends, while those of comparative settlements often travelled. Thus, they reduced the environmental contamination, especially that of carbon dioxide, but also rendered a service to the society: They avoided the stress of congested roads for themselves and especially their children and with this contributed to health in general. An architect had created an environment with positive answers to our problems.

When coming to architecture and building, we often face questions, what material to choose. Anything goes. If Carrara marble is wanted for a prestigeous building, it will be shipped from Italy to Singapore - like fresh flowers, which are flown daily from South America to Germany. From a recent thesis we know, that a cup of yoghourt may have travelled a total of 5000 km in Germany, before ending on a table in Berlin. There are enough trucks, enough roads and enough cheap fuels to choose the cheapest or otherwise qualified product - all at the expense of our environment.

This also applies to building materials. Formerly, only materials were used, which were known and available nearby. This means, very little energy was required for building, except 'man-power'. Today we use heavy machinery for excavation and processing, energy for transport and construction.

We call this the energy content of materials, which will have to be added to the total energy, which a building consumes in its life-time. In view of environmental suitability we should assess the properties of a material also in terms of thermal qualities, toxic emissions, re-use-qualities or recycling and, finally, also from the point of comfort, as felt by the user.

Meanwhile, the disposal of waste building materials has become a considerable financial problem, especially, when harmful matters like asbestos or chemical products have to be disposed of. This aspect will, in future, determine much more the choice of materials, than this has been the case so far. The automobile-industry has taken first steps already.

Good architectural design is not a linear process, but rather one of advancing and stepping back again for reflection and control. In this, the consideration of climate plays an important role.

This is not new. The Greeks already planned their cities remarkably well in this respect. That dates back to the 5th century B. C. In recent years of cheap energy, however, we took liberty to ignore this, because we could use energy to balance the mistakes of poor planning.

And often is it not limited to the architect's decision, when the client insists on a facade or roof construction, which he considers modern and prestigeous - no matter, how much energy will be used for overdimensioned air-conditioning, to make the place habitable.

Since the days of the pioneers, wooden houses have a tradition in North America. But large areas of the continent have a continental climate, i. e. hot summers and cold winters. In such climate, materials with good heat storage capacity are preferable. Light construction with timber is cheaper, but requires much more energy for providing indoor-comfort, which in the life-span of a building is neither economical nor ecological.

Maxwell Fry, one of the pioneers of tropical architecture after World War II said: "The neglect of building with climate is a kind of suicide. Climate is a decisive factor in life".

Man tried, from his very beginnings, to improve upon climate conditions of his abode. The example of climate-conscious Greek town planning has been mentioned. Exceptional systems for the improvement of indoor-climates were developed by the Persians. They used wind towers, underground air ducts and water for lowering the air-temperature.

Traditional architecture and settlement patterns in arid islamic regions were, for several reasons, better adapted to overall conditions, than modern, i. e. western architecture and planning.

It seems somewhat contradictory, that the neglect of long experience in building started just at that time, when a scientific base was laid for correct planning with climate.

The Bauhaus and the Charter of Athens, which requested the separation of work and leisure, had their time in the 20ies and 30ies. After World War II their philosophy conquered the world with the so-called 'International Style'. This was considered modern, because it originated from the successful industrialized countries of the West and eliminated, step by step, regional architectural patterns, which had grown in agreement with socio-cultural value-systems and in harmony with prevailing climatic conditions.

At the same time, the building boom in newly independent or wealthy oil-exporting countries generated extensive research on building with climate.

Foundations for this were laid already in 1923, when Houghton and Yaglou determined the human comfort zone and established the interdependence of dry and wet temperature with air-velocity as 'Effective Temperature'.

For warm countries, the aim was, to improve upon the indoor-climate. In temperate climate, i. e. in the Industrialized Countries, the aim was, to reduce the heat-losses through the building envelope and to find alternatives to fossile and nuclear energies. This was generated by sudden problems of oil supplies in the 70ies.

In addition to the need of applying the rules of good planning with climate in warm countries, the need to have access to alternative energies is becoming more and more important today for Developing Countries.

In warm and temperate climates we can choose between active systems, i. e. employing air-conditioning or complete control-systems called 'Intelligent Building', by which modern electronic devices control all changes in temperature, humidity and light for necessary reaction.

It is possible, to combine active and passive systems into a hybrid one, which combines both or selects, as the case may be. This can save additional energy, but is more costly to install.

Air-conditioning is expensive and consumes much electricity. If correctly planned and well maintained, it saves the architect headaches in planning - at the expense of the user and the environment. There are many cases, of course, where air-conditioning is indispensible, e. g. modern offices with electronic equipment, operating theatres, libraries.

In contrast to active systems, which provide an artificial climate, passive systems try to make the building a balancing organism, i. e. using the cycles of climate or natural phenomena for the improvement of indoor-climates.

In dry-hot regions we use the heat-storing capacity of specific building materials to keep out excessive heat in daytime and to use it for warming the interior during cold nights.

In warm-humid regions, where day- and night-temperatures show little difference, we use light materials and maximum ventilation.

The application of these basic rules is neither difficult nor new. They have given, until recently, whole regions their special architectural identity.

For all building in warm climate the protection from solar radiation is most important. We should not accept evasive statements like 'the overhanging roof will give shade' any longer. Solar control can be calculated precisely for any latitude, any day and any hour.

As mentioned before, generations of the past developed admirable solutions with their available resources in their reaction to climate. In this, they never developed a national architecture, but rather a regional one - always depending on the local conditions.

In the younger generation, we observe today a change of mind, a reconsideration of former values in regional architecture. Careful study of achievements of the past in combination with requirements and possibilities of today will pave the way for a positive development, which does not mean to misunderstand local identity as the copy of decorative forms of the past.

Research in building with climate and alternative energies will play an important part in this development - for the benefit of man and his environment.

Energy Saving Building Materials, Design Principles and Construction Techniques for Tropical Climates

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1. Introduction

Ecological building concepts – and particularly the reduction of energy consumption in buildings – are vital requirements in building construction today, as we have to economize on the natural resources of our planet. When considering low energy concepts, we usually think of reducing energy expenditure during the occupation of a house. But it is equally important to take into account the energy consumed long before, namely in the production of building materials and in the construction process. Linked to this energy consumption are two significant ecological aspects: environmental pollution and loss of oxygen.

These considerations show the importance of promoting ecological architecture, the key aims of which are

- to save natural resources,
- to reduce pollution,
- to reduce energy consumption, and
- to create comfortable and healthy living conditions.

This paper, therefore, deals with the energy consumption of various building materials and the environmental consequences, as well as some innovative, ecological design principles and construction techniques suitable for tropical climates.

Building material	kWh/m³	kWh/kg
burnt clay bricks (solid)	1140	
burnt clay bricks (perforated)	590	
porous lightweight bricks	400	
sand lime bricks	350	
cement		1
concrete	500	
precast concrete	800	
earth	5	
timber	600	
chipboard	1100	
mineral wool	100	5
glass wool	150	5
flat glass	15000	6
steel (plates)	6100	7.7
aluminium (sheets)	195000	72.5
PVC	12800	9.5
polystyrene foam	470	19

Table 1: Energy required for building materials production in Germany (Ref. 1)

2. Energy consumption in building materials production

The production of industrially manufactured building materials and semi-finished products uses up an extreme amount of energy. As shown in Table 1, 1 kWh of energy is required to produce 1 kg of cement. For steel we need about 7 kWh, and for aluminium more than 70 kWh per kg. In terms of volume, 1 cubic metre of concrete uses up 400 to 800 kWh, and solid bricks as much as 1140 kWh, whereas earth needs only about 5 kWh per cubic metre.

This means that solid bricks need twice as much energy as concrete, which in turn requires about 100 times as much as earth. This is because the cement in the concrete not only consumes a lot of energy in burning the raw clay and lime, but also has to be pulverized, packed and transported. On the other hand, for the production of air dried earth bricks (adobe) or for rammed earth construction, we need no energy for the material itself, and very little for transportation and handling on the site.

3. Energy consumption and pollution

Even more problematic than the high consumption of energy for the production of building materials are both the surprisingly great loss of oxygen and the increase of pollution – two aspects that have severe consequenses for our existence on this planet.

While – ecologically speaking – our energy resourses require thoughtful handling, in economic terms it can be said that the energy costs will have to be paid by the ultimate consumer. The costs for the loss of oxygen and the envioronmental pollution, however, have until now not been paid by those responsible, but will have to be paid by future generations.

At present, only very little data is available on these aspects. But we know, for instance, that in Germany the production of 1 kWh of electricity releases 5.5 g of SO_2 and 2.5 g of NO_X and other polluting particles into the atmosphere. The two substances mentioned are mainly responsible for "acid rain" and thus for the dying of our forests.

As examples of oxygen consumption: the production of one tonne of steel requires 50 cubic metres of O_2, while aluminium requires 10000 cubic metres of O_2 per tonne, ie 200 times as much. The consumption of oxygen results in the production of CO_2. During the last 100 years, the content of CO_2 in the atmosphere rose from 0.022 to 0.0333 percent, which has led to a considerable rise of the average temperature of our planet.

4. Building with earth

The environmental pollution and energy wastage that occurs in conventional building material production and the construction process can largely be avoided if, for example, earth in the form of blocks or rammed in situ is used instead of burnt bricks or concrete.

Earth, a mixture of sand, silt and clay, is a natural building material used all over the world since ancient times. Adobe bricks (sun dried bricks from clayey soil) and rammed earth have been known for at least 8000 years. For instance, the core of the "pyramid of the sun" in Teotihuacan, Mexico, consists of two million tonnes of rammed earth. The "Great Wall of China" was originally built of rammed earth, and only later covered with stone or brick.

Earth has two decisive disadvantages in comparison to industrial building materials:

- it shrinks when it dries, and
- it must be protected against moisture.

Both disadvantages can be avoided by constructive means.

At the same time, however, it must be said that earth has some fundamental advantages over conventional building materials:

1. The building process requires very little energy and causes no pollution.
2. Earth creates a comfortable climate within the house. It balances temperature fluctuations (in summer an earth house is pleasantly cool, in winter comfortably warm) and – even more important for human health – it balances the moisture content. Earth absorbs 30 to 50 times more humidity than burnt bricks (depending on the degree of firing) and also emits it relatively fast.

3. Earth is usually available on or close to the building site, and the material excavated for the foundation or cellar can be used as building material.
4. Earth is always reusable, as it is applied unburnt.
5. Earth requires hardly any capital input (machines, buildings, etc) and is suitable for "self help" constructions with unskilled labour.
6. Earth reduces building costs.

Earth – in Europe almost forgotten as a building material after World War II – is being rediscovered today, especially by owner-builders. Traditional techniques of building with earth are very labour intensive. However, intensive research on these technologies are being conducted since 12 years at the Building Research Laboratory of the University of Kassel in Germany, where several mechanized earth construction methods have been refined or newly developed, and are waiting to be applied on a larger scale.

Fig. 1: Production of compressed soil blocks in India, using a locally manufactured block press (Balram), which can be operated by unskilled workers.

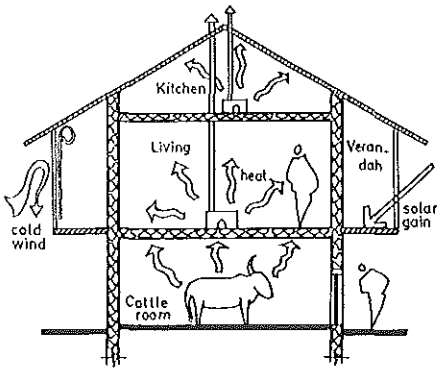


Fig. 2: Some typical passive design elements in a traditional rural house in a cold and cloudy region of India (Ref. 2)

5. Design principles

One of the main functions of a building is to provide a comfortable indoor climate for its occupants. This means influencing the temperature, humidity, air motion, lighting and acoustics. In conventional buildings, these are often controlled by mechanical means, which are expensive to buy, install and operate, consume a great deal of energy, can be noisy and often cause unhealthy conditions for the users.

Passive building design aims to avoid all these problems by natural means of climatic control, whereby, for instance, the following aspects are taken into consideration:

- orientation of the building
- shape of the building
- adaptation to topography
- shading
- heat insulation
- heat storage
- evaporation cooling
- ventilation
- humidity control by moisture regain

In cases where a passive system uses technical equipment that requires only a small amount of energy compared to the energy saved, the system is still called "passive". If there is a significant energy requirement, the system is called "hybrid" (mixed system).

Passive Design		Climatic Zone			
Principle	Concept	Hot-Dry	Warm-Humid	Moderate	Composite
Reduction of solar heat gain	Orientation	small walls facing east and west		bedroom facing north	
	Small surface-to-volume ratio	compact plan, low wall height	compact plan, low wall height		compact plan, low wall height
	Shading by neighbouring structures	row housing, high compound walls		clustering of houses	clustering of houses, courtyard
	Shading by vegetation	large trees			deciduous trees
	Shading by overhangs	overhanging roof	overhanging roof	fixed shading elements for windows	vegetation on façade
	Small openings	no windows			small windows
Reduction of internal heat gain	Heat from kitchen	outdoor kitchen	outdoor kitchen	outdoor kitchen	outdoor kitchen only in summer
Reduction of heat transmission into the interior	Thermal insulation	insulating roof, thick walls	insulating roof	insulating roof	insulating roof
	Reduction of air infiltration	wind breaker / fence (against hot winds)			moveable curtains on windows
Increase of heat loss	Ventilation	courtyard effect, wind catcher, solar chimney	courtyard effect, openings close to roof, porous walls and roof, windows facing wind direction, ventilation under raised floor,	smoke oulet / ventilation duct in kitchen	courtyard effect, separate shaded pavilion for sleeping, high level openings
	Evaporation	vegetation, sprinkling water			vegetation, sprinkling water

Table 2: Examples of passive building design concepts and elements for four different tropical climatic zones

In order to develop guidelines for passive building design, it is necessary to differentiate between the various climatic zones, which can be very diverse and require quite different design concepts and elements. The above table gives a few typical examples of these, taken from an Indo-German research study, conducted jointly by the Centre of Energy Studies of the Indian Institute of Technology, New Delhi, and the Building Research Laboratory of the University of Kassel.

6. Advantages of vault and dome structures

A vault or dome covered space shows several advantages in comparison to a common rectangular room covered by a flat roof:

- For a constant volume, the height of a dome or vault covered room is higher, giving more thermal comfort by more effective cross ventilation (high windows in the end walls of vaults) and better ventilation by the increased stack effect (release of warmer air through skylight openings in domes, replaced by cooler air via lower inlets).
- Skylights on vaults and domes not only provide 4 to 5 times more light per unit area than low windows on vertical walls, but also provide a more even distribution of light.
- As less window area is needed, heating and cooling loads are reduced.
- The shape of vaults and domes can be optimized so that no bending moments and no tensile ring forces will occur. This leads to cost savings, as no reinforced concrete or steel structure for stabilization is needed.
- With special construction techniques, no shuttering and no skilled labour is required, thus saving construction time and costs.

7. Refined Nubian vault construction technique

The Nubian vault construction technique is a several thousand year old building method, by which buildings can be roofed without supporting formwork during the construction process, simply by placing flat bricks in inclined arches, such that each brick rests on the layer below, passing the compressive forces in a curved line within the thickness of the structure.

Based on tests of the Building Research Laboratory, the amount of mortar as well as the construction time can be reduced by using bricks of 20 cm length with the width tapering from 18 to 20 cm, which reduces the volume of the mortar joints.

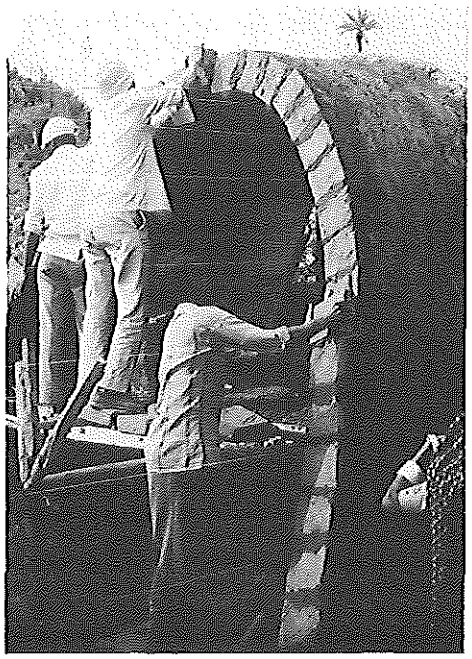


Fig. 3: Refined Nubian vault construction technique, Mt. Abu, India (Design: G. Minke)

On the other hand, the vault thickness of 20 cm was found to be sufficient for spans of 3 to 4 m. By installing a system of guide strings, which are self correcting by counterweights, a greater accuracy (and therefore stability) and a considerable reduction of construction time was achieved. This technique has been applied in several projects in Germany, Hungary and India (Fig. 3).

8. Structurally optimized dome construction technique

The traditional Nubian dome construction technique, with which a spherical surface can be achieved, has the disadvantage that tensile ring forces occur around the lower part of the dome. This means that larger domes tend to collapse (as has happened before on several buildings), if they are not stabilized by reinforced concrete ring beams, by steel strips or by heavy buttresses.

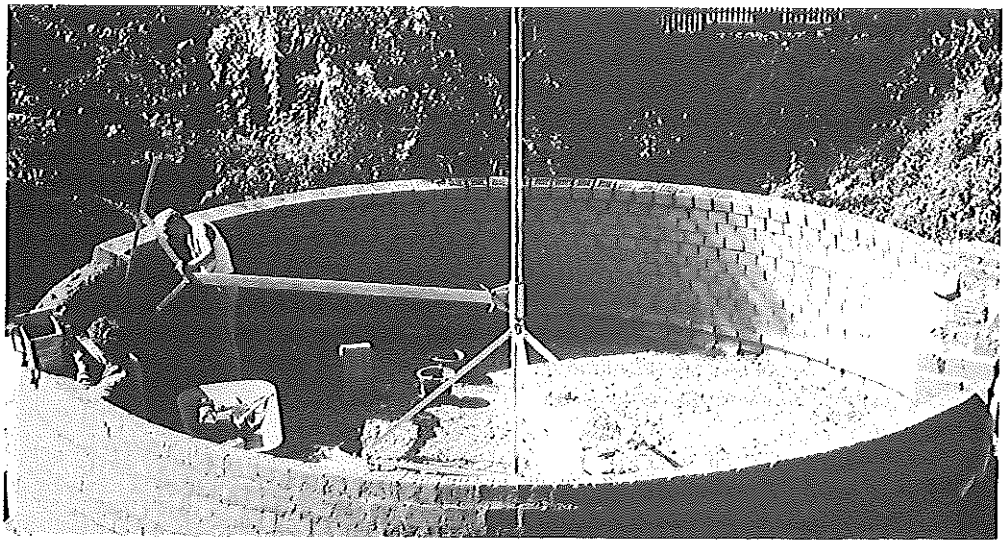


Fig. 4: Experimental dome constructed at the University of Kassel (Design: G. Minke)

At the Building Research Laboratory, a new technique was developed utilizing a rotation guide, allowing the soil blocks to be placed with great accuracy according to the "optimum" form, calculated by a computer programme, which guarantees that no tensile ring forces occur within the surface: all dead loads are transferred under compression into the foundation. A dome of 6 m height and free span of 7 m was built in 1992 at the experimental building site of the University of Kassel (Fig. 4). The thickness of the dome structure is only 20 cm, built with tapered soil blocks that were produced in a brick factory by an extrusion process and used unburnt.

9. Two examples of energy efficient, climatically appropriate building designs, using local materials

a. Office building in New Delhi, India

The 115 m² vault and dome structure of the Indian Institute of Technology (I.I.T), New Delhi, provides office and laboratory space for a research group of the Centre of Energy Studies (Figs. 5 and 6). The building was built in 1990 within a research and development project, financed by the GTZ (German Agency for Technical Co-operation, Eschborn), with support from the International Bureau of the KFA Research Centre Jülich, Germany; I.I.T. New Delhi; and the Building Research Laboratory of the University of Kassel. (Design: Gernot Minke; collaborator: R. Muthukumar; Energy concept: N. K. Bansal).

The three vaults were built according to the refined Nubian vault construction technique described above, with unburnt soil bricks, made from the soil excavated for the foundation. Similarly, the three domes were constructed according to the newly developed technique, using rotation guides. The stabilized soil blocks were produced by a manually operated block press.

The section of the domes is similar to a catenary or elliptical curve. Only the large dome with a clear span of 5.4 m needed a small ring beam, as it was placed over octagonal vertical walls, which serve as projection and exhibition surfaces. Within the small domes all loads are transferred under compression into the foundation, avoiding the use of concrete.

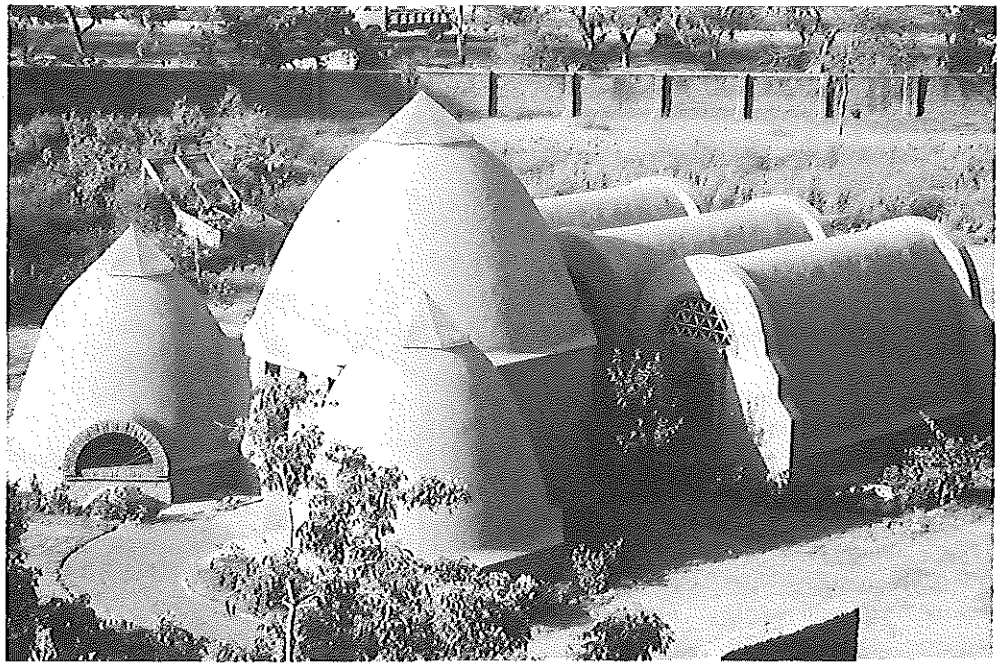


Fig. 5: View of the completed building at the Indian Institute of Technology, New Delhi. (Design: G. Minke)

Fig. 6: Applying the water resistant rendering, a mixture of silty soil, sand and cow dung.

A significant feature of the building is the avoidance of reinforced concrete lintels above doors and windows, by corbelling the bricks, that is, allowing the bricks on either side to project inwards on successive horizontal courses until they meet at the top.

In order to protect the building against rain, a cow dung mud plaster was used, which had been optimized in prior tests by the Building Research Laboratory. The mixture comprised one part silty soil, one part cow dung and one part coarse sand. After mixing the cow dung with water, it was important to allow it to ferment for one day. The dry plaster was painted (flooded) with a hydrophobizing agent and withstood the monsoon without any damage.

b. Farm house in Wazirpur, India

The single storeyed house with a floor area (including veranda) of 206 m² is surrounded on the east, north and west sides by earth berms, while the south side overlooks a small lake, which is a central visual element of the

landscape design, acts as a climate modifier, and stores rainwater in the monsoon for household water supply and irrigation.

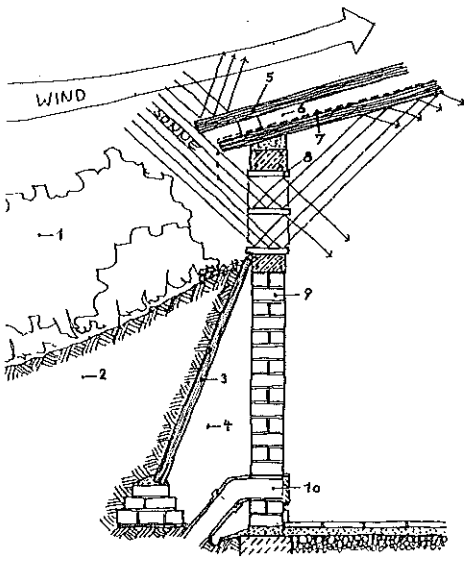
The building was designed by Gernot Minke, in co-operation with DAAT, New Delhi, and will be completed in 1994. It incorporates several passive design elements (as shown in Fig. 7), which provide a comfortable indoor climate and at the same time require far less energy than conventional buildings.

The main building materials are handmade mud bricks and locally available sandstone slabs. Loadbearing stone columns support stone beams and slabs to form slightly dome shaped roofs, which consist of two stone slab layers and an air cavity. Air cavities as thermal insulation are also provided between the earth berms and the outer walls.

10. Conclusion

The technologies and examples of projects described in this paper attempt to show new ways of counteracting the negative effects that most conventional building systems have on the environment. True, the building industry is not solely responsible for the wastage of the limited natural resources, for the pollution of the atmosphere and for the alarming climatic changes that are taking place, but considering the dramatic increase of the world population and the immense demand for buildings almost everywhere, the building industry is becoming an increasingly important factor.

Therefore, every effort to save energy, avoid environmental destruction and at the same time improve the people's living conditions and health should be undertaken under all circumstances. While all this is achieved by the technologies described above, practical demonstrations have also shown that they save considerable costs in the production of the building materials, in the construction process and also in the long term use of the buildings.



1 Shrubs to deflect winds
2 Earth berming
3 Stone panel
4 Air cavity for thermal insulation
5 Light coloured stone slabs for sun reflection and weather protection
6 Air cavity
7 Bituminous roof sealing
8 Light sandstone louvres for shading, light reflection and burglar proofing
9 Exposed soil block masonry for heat storage and balancing indoor air humidity
10 Climatization by earth tunnel system

Fig. 7: Typical outer wall section of the farm house in Wazirpur (Design: G. Minke)

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KFA Julich - AEA Cairo
Joint Seminar on Environmental Research and Development

NEW APPROACH FOR DESERT DEVELOPMENT

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Abstract

Desert development is becoming an important and integral part of Egypt's economic strategy. Several new cities have been established in desert areas by the Egyptian government, in order to attract people away from the over-crowded urban centres and provide new housing and investment opportunities for them. However, such ambitious undertakings call for new development concepts for building and living in desert environments. Since the Egyptian Atomic Energy Authority saw the need to expand its research and administration facilities and to develop a new housing and recreational area for its staff at the Inshas Research Centre, on the barren desert strip in the northern portion of the site, it was faced with the same problems as the new cities. Hence this was seen as an opportunity to demonstrate examples of desert architecture and technical service systems, based on Egyptian traditions coupled with innovative, environmentally appropriate technologies.

This paper presents a general outline of the project, highlighting the various environmental aspects of the design concept, especially in terms of innovative, energy and cost efficient architecture, renewable energy systems, environmentally acceptable water and waste management and so on. The entire project is being conceived as a demonstration of a new approach to desert development, and will hopefully set an example for other countries of the Northen Africa and Middle East regions.

1. Introduction

The Egyptian Atomic Energy Authority (A.E.A) in Cairo is planning to develop the northern portion of the AEA Inshas site, in line with their future research and development programme activities.

The Inshas Science City Project (ISC), is located in the Inshas Research Centre, about 40 km northeast of Cairo. This project is an essential component of the AEA desert development programme, making use of AEA's classical fields of expertise and introducing new technological developments, e.g. renewable energy , ecological farming and related fields.

2. Project aims

This project would be a prototype and an experimental to serve as a real example for desert community that can be built in the desert, the following are some of the aims of this project:

a) To develop the northern portion of the AEA Inshas site over the next 5-10 years, incorporating innovative, energy efficient architectural design concepts and technologies as well as environmentally appropriate technical service systems (energy and water supply, waste disposal and recycling systems, ecological farming, etc).

b) To design and build some facilities for research and development, facilities for the accommodation of AEA staff and foreign guests, as well as facilities for recreation and health care, including administration and supporting services.

c) To build these facilities in traditional Egyptian style, using local design features and building materials with a special view to passive design concepts and elements and also to energy efficient building design.

d) To use these facilities as a centre for the Demonstration of Ecological Architecture and Appropriate Technologies, which will function as an information and documentation centre for the entire Northern Africa and Middle East region, equipped with development and training facilities for appropriate technologies in building

construction and supporting technical systems, such as renewable energy systems, water supply and waste management, ecological farming and the like.

3. Scope of the project

In order for Inshas Science City project (ISC) to attain its aims the following actions are made:-

1) Setting up of a co-operation project between AEA and KFA, Julich in Germany.

2) The master plan of Inshas project made after site survey was conducted including topography, seismic, ground water, resources availability, meteorological data, vegetation, excess to the site, etc. (Fig.1).

3) Proposals of the project layout were made by prof.Christians and his group in Berlin University to get such ideas before we will go to the final design (Fig.2).

4) Two buildings of the project are already completed by 1993, the Desert Agriculture Laboratory building (D.A.L) and the Pilot building (Fig.3). The design of these building was based on Egyptian traditions coupled with some solar passive concepts and appropriate technologies.

5) An on the-job training was conducted for 15 AEA staff members (engineers, technicians, draftsmen and workers), and 4 representatives engineers from the New Valley governate and staff member of the construction contractor to demonstrate innovative dome construction developed at the building Research laboratory of Kassel university in Germany (Fig.4).

4. Towards architecture aspects of the project

The increasing population, growing urbanization and industrialization in Egypt have contributed of a scenario of rapid growth in energy demand. Therefore, the issues relating to energy availability and energy efficiency have been brought into sharp focus. In this context it has been noted that most countries spend nearly 15 to 20 percent of their total energy budget in the

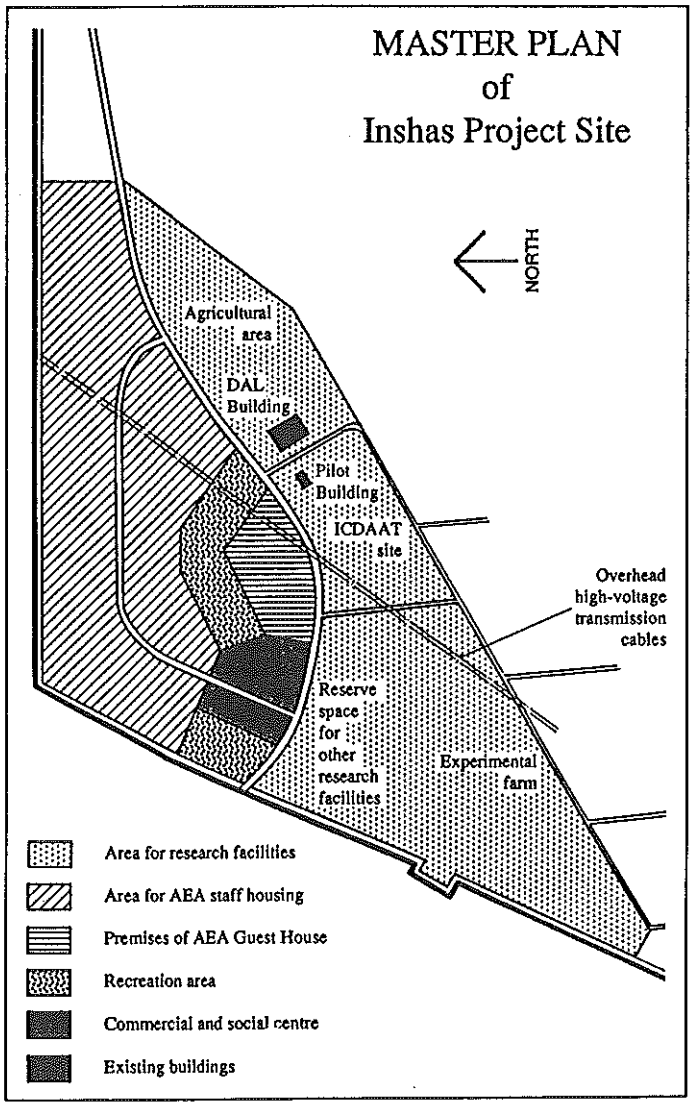


Fig.1 Master Plan of Inshas Project, made by S. Algohary, K. Diab, and K. Mukerji.

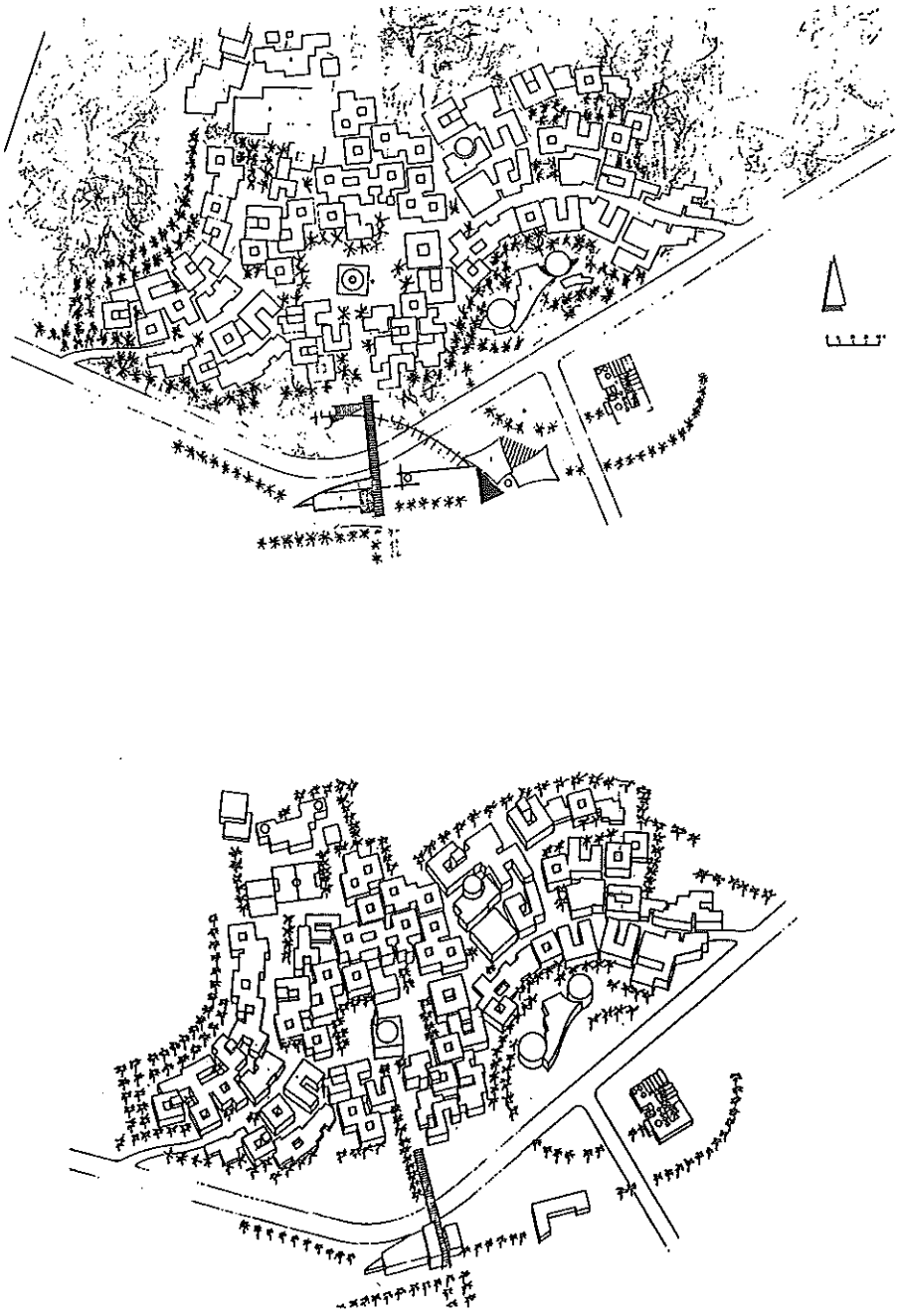


Fig.2 Layout Proposal, made by prof. Christians and his group in Berlin University.

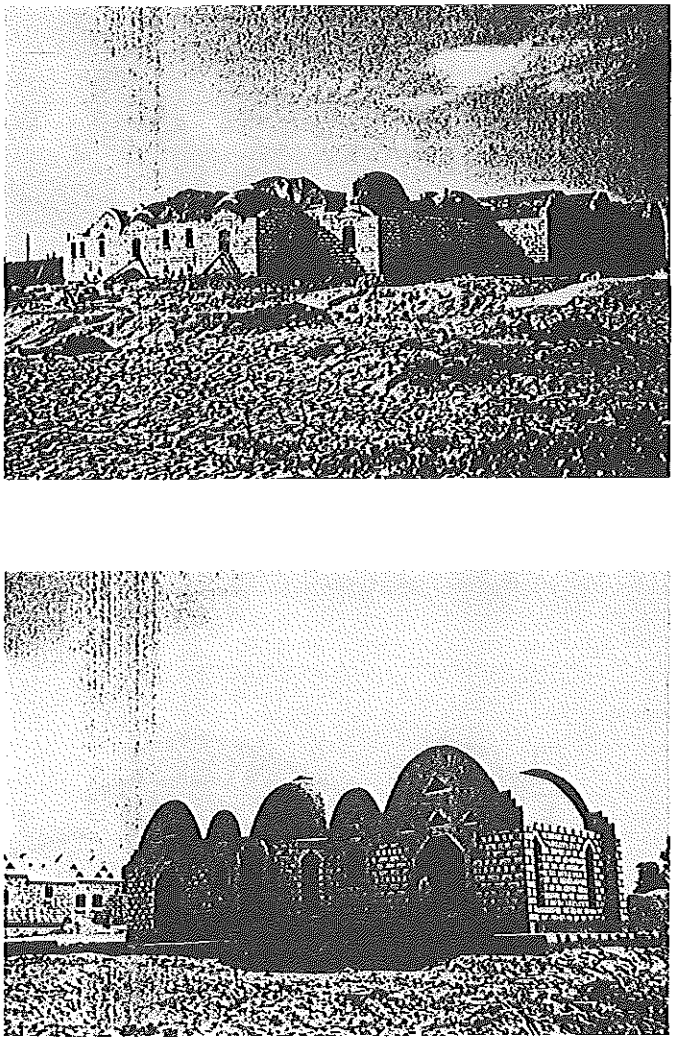
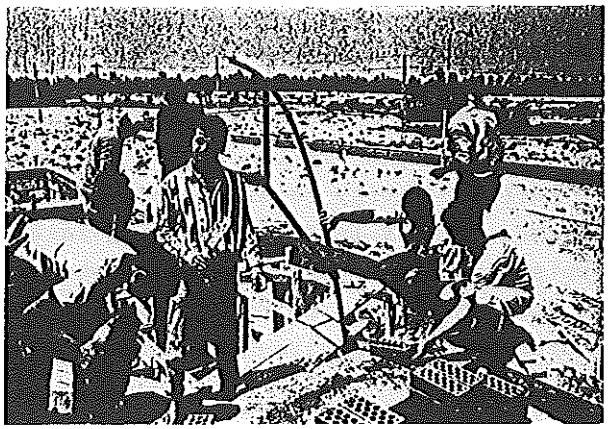
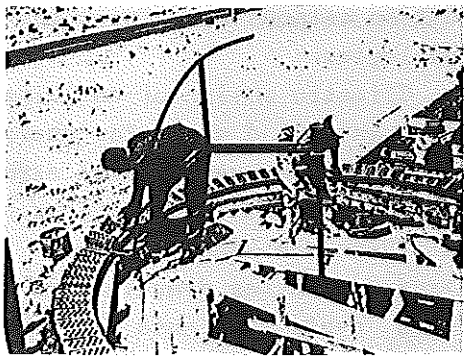


Fig.3 Views Toward D.A.L. Building, and the Pilot Building.





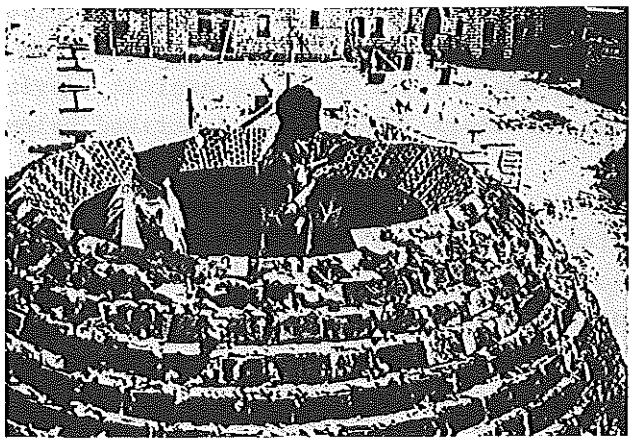


Fig.4 An on the-Job Training for AEA Staff.

building materials industries.

The close connection between a building's energy use and environmental damage arises because we still look to imported methods and techniques to meet our energy related needs. The use of these imported approach has largely meant introducing into the Egyptian systems, concepts, designs and materials which are followed in the so called more advanced countries. This has done a severe damage to our resources and our environment and above all; quality of our life.

For that, we have to think again about our approach, to use our resources and also to look for our Egyptian culture and tradition methods coupling with all innovative and appropriate technologies.

Climatic design of buildings based on natural agencies such as daylight, wind and solar energy can be considered an imperative approach for saving wasteful expenditure of energy, and on the same time as climatic conscious architecture.

There are many options available to the designers for cooling or heating domestic and non domestic buildings which can help to avoid the use of mechanical air conditioning while achieving comparable comfort levels with much lower energy use consequent savings in atmospheric pollution. Some of these options are totally passive, requiring no mechanical consistence, while others may need a relatively small input from mechanical devices such as fans or pumps. Some of these options are described below:

4.1 Orientation

Building in different orientations intercept different amounts of solar radiation, depending upon the surfaces exposed in different directions. Good orientation is essential for an energy efficient building design. It is noted that with a N-S orientation we can minimize the solar radiation intercepted by the walls in summer, and maximize the solar radiation intercepted in winter.

4.2 Buildings Design (concepts,forms, layouts)

By the change of form of the buildings, it is possible to modify the solar radiation intercepted by different surfaces of the building.

Traditional neighborhoods comprise mainly indigenous courtyard houses. In concept, these structures are built contiguously (back-to-back and side-to-side) forming a series of blocks of mass buildings of various sizes and different shapes. In layout, these neighborhoods are characterized by compact layouts and organic growth with different narrow and wide roads separating the blocks and buildings and have a hierarchy of their own spaces reflecting the size of these blocks. In form, the mass of houses is generally two stories high, this does not mean that the houses are uniform in height but it relate to the size of the houses which in turn is related to the size of the plot and the human scale.

It is noticed that such concepts, layouts and forms are optimum for the desert communities. (Fig.5) shows the plan and perspective of the proposed neighborhood unit which reflecting some of these concepts and design aspects.

4.3 Shading

Solar radiation and unlike heat radiations, are of short wave lengths and can be protected against by shading. Therefore, to reduce the heat flux entering buildings, a very simple method is to provide adequate shading so that the amount of radiation absorbed by the outside surfaces is minimized. Surface shading can be provided as an integrated part of the buildings by sunshades or it can be provided separately by deciduous trees.

(Fig.6) shows the section of the guest house building where the photo- voltaic panels were used as a sunshades beside its purpose for power generation.

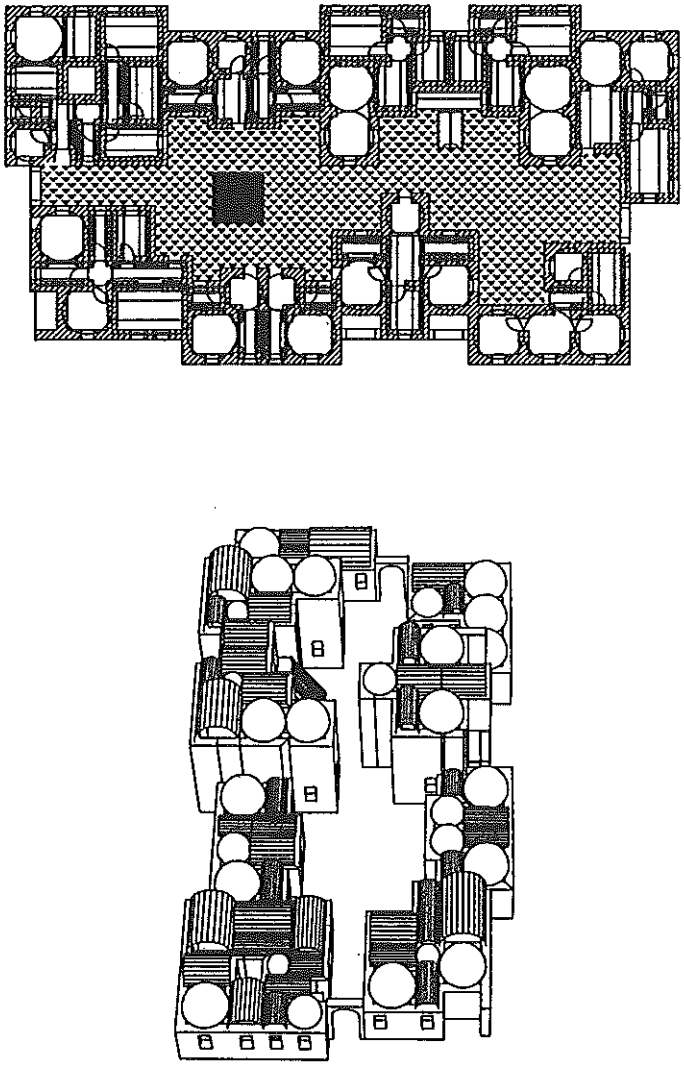


Fig 5 Plan and Perspective of the Proposed Neighborhood.

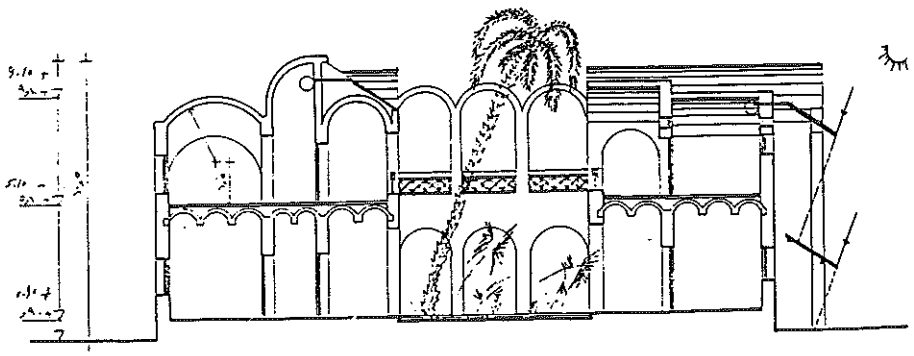


Fig.6 Section of the Guest House Building.

4.4 Courtyards

The concept of a cluster built around a courtyard was adapted from its use in ancient time.

The internal courtyard reaching implications, these are directly related to the following aspects:-

1) Urban design and three-dimensional form of architecture.
2) Passive solar element, which control of micro-climate.
3) Culture value of the region.

(Fig 7) shows the plan of the guest house building where the courtyard integrated in the design.

4.5 Massive Walls

Massive walls of bricks or stone are favorable for hot climate areas, in addition to their insulating properties,

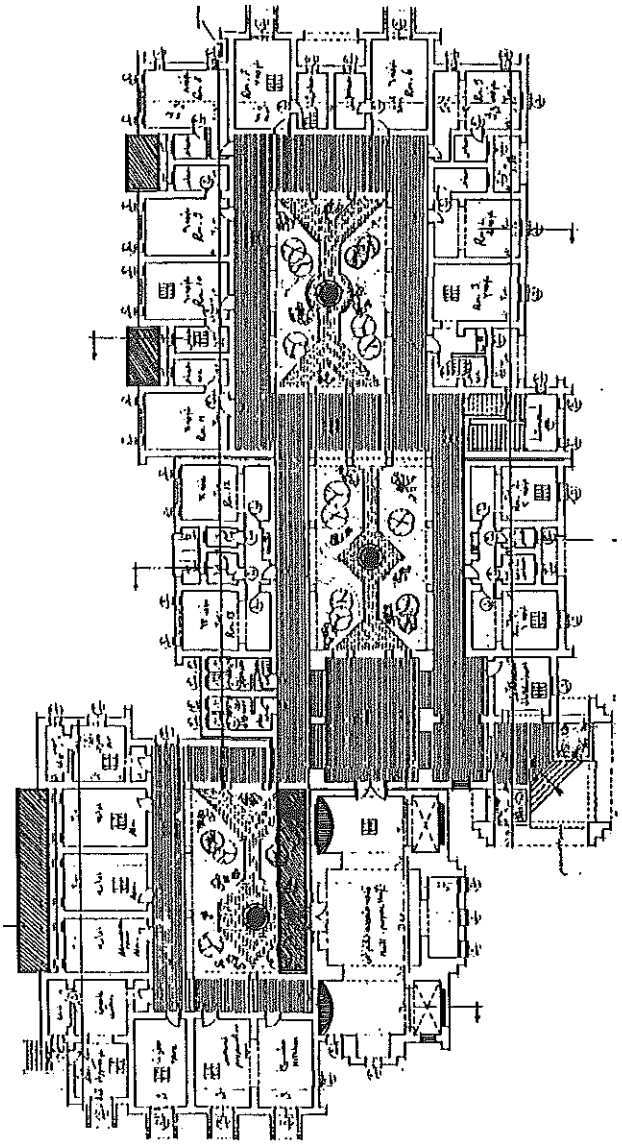


Fig.7 Plan of the Guest House Building.

function as heat reservoirs. The main consequence of this is a minimization of temperature change inside the building with respect to the outside temperature.

In Inshas project, natural white lime stone was used in construction of bearing walls because using silt in production of bricks has been stopped by the government, and the result is satisfactory for its insulation properties.

4.6 Domes and Vaults

Summer sun in the desert areas is perpendicular to the roofs of the buildings for few hours during most days, these hours is enough for the roof to become a heat source. For that maximum attention for roofs is required.

Curved roofs (domes and vaults) were used for roofs construction because it has a large convection heat transfer surface; whereby it is more easily to cool. (Fig 8) shows the shade percentage over a dome in example in Iran, which shows that at any time of the day there is shade percentage over the dome.

4.7 Solar Chimneys

Solar chimneys make use of solar heat to reinforce natural air convection. (Fig 9) shows some types of the solar chimney, the concept depends on that the black-coated chimney is heated during the day and so is the air inside. The latter then expands and rises, tracking the interior air up and out. This is a self-regulating system and the hotter the day, the faster the air motion.

4.8 Earth-air Tunnel System

The use of earth-air tunnels to heat or cool a buildings is an ancient concept which has been revived by practitioners of solar passive architecture. Earth-air tunnel can function as an isolated passive system. The main idea depends on that the temperature of the ground, a few meters below is almost constant throughout the year. The system consists of air ducts situated

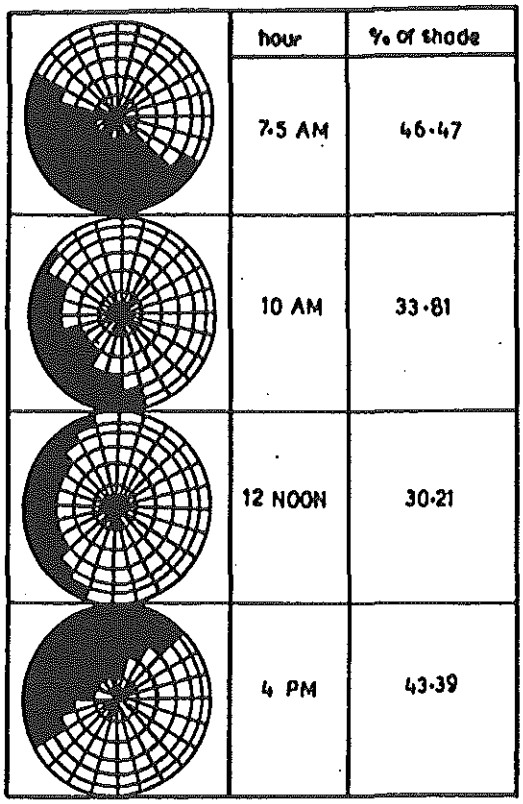


Fig.8 Shade Percentage Over Dome on September, 22, Iran
(A. Sabzevari, A. A. Golneishan)

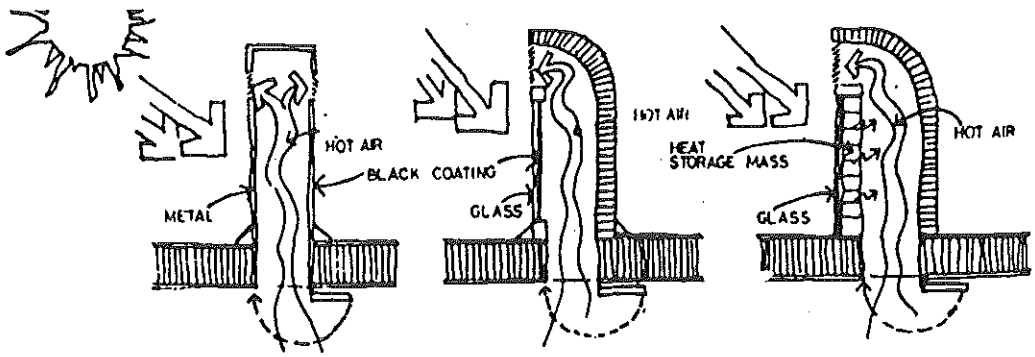


Fig.9 Different Types of Solar Chimney.

under the ground through which air is piped to the building. It is noticed that the air will get cooled in summer and heated in winter by conduction of heat to the earth in summer and vice versa in winter (Fig.10).

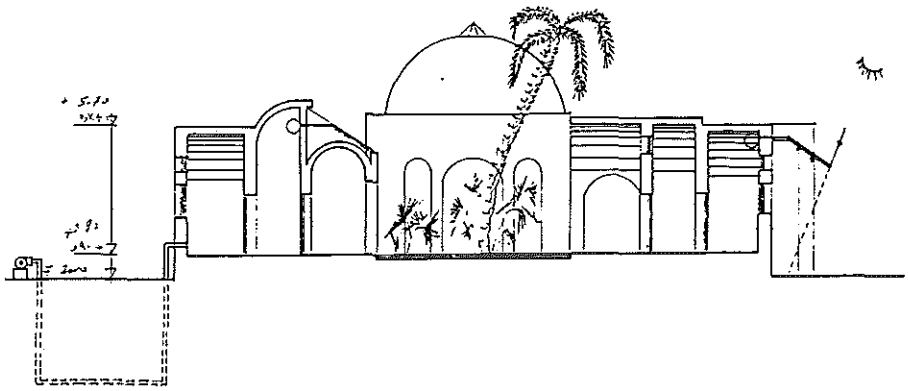


Fig.10 Section of the Guest House Building Shows the Earth Air Tunnel System

4.9 Daylighting

In Egypt, when sunlight is available for greater part of the year, daylight of building interior should be an important design factor, windows offer one of the best methods for providing natural lighting because the windows are almost always incorporated in the building design. Artificial lighting is practically independent of any constraints; daylighing, however, strongly depends on the eternally given conditions and its control is possible only by proper orientation, placement and sizing of the windows.

Finally, the previous techniques are not only the available solar passive concepts but their also exist many other elements such as wind towers, fountains, insulation and color of the buildings, etc.

5. Towards Renewable Energy technologies

There is now little doubt that new and renewable energy technologies in one form or other will play significant role in the future energy supply systems of a large number of countries in the developing world. For that, we have to consider this issue in our approach for desert development.

There are a lot of renewable energy technologies which can be implemented in the new sites some of them are:

- Solar water heating system in industrial and domestic purposes.
- Solar air heating and drying systems.
- Solar photo-voltaic system (SPV) for water pumping.
- SPV lighting system.
- SPV power plant.
- Wind mills for water pumping.
- Wind generator.
- Bio-gas plant for heating and cooking.

Experience in the many countries over the past decade in implementing these various new energy technologies based on local resources can be viable alternative to many commercial sources of energy both in rural and urban areas.

6. Towards Waste Management

One of the serious problems affecting our cities and also new cities is difficulty of eliminating garbage in a simple and economical way.

According to a paper by K. Mukerji (1), such a system for waste disposal is suggested (Fig.11), It is noted that liquid waste can be passed to biogas generator to produce methane for power and light purposes, also the sewage can alternatively be recleaned by sedimentation and coagulation, and then passed

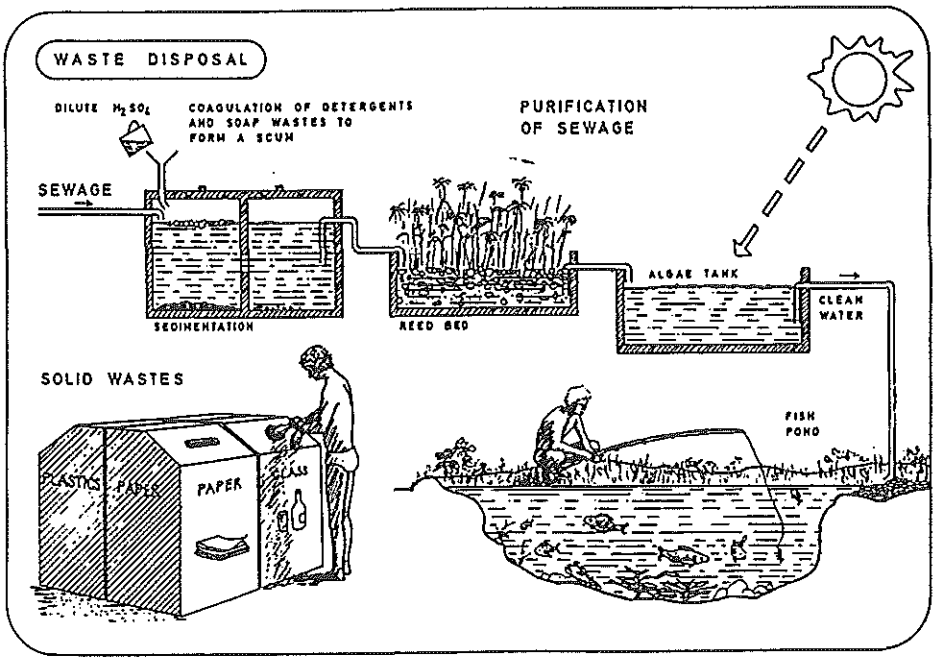


Fig.11 Proposal of Waste Disposal, by K. Mukerji.

through reed beds, algae tanks and fish ponds to purify the water, which is enriched with nutrients and thus ideal for watering plants and on the same time for algae and fish production.

With regards to solid wastes, separate containers for the collection of composible garbage, paper, glass, metals, and plastic are favorable. These materials can be used profitably for recycling, which conserves raw material and saves a great deal of energy, apart from preventing unnecessary waste and pollution.

7. Conclusions

Some practical and useful ideas are being put forward as conclusion of the presumed work to provide such approach for desert development.

1) The new communities in the desert should offers a good quality of life to be attractive enough to encourage migration of people from the over-crowded urban centres to the desert areas.

2) Desert development must focus on integrated and sustainable systems related to the problems and resources of each desert area.

3) Architects and designers have available a multitude of ways of using nature's help to achieve an acceptable climatic ambience through sensible and wise architectural design.

4) The best opportunities for improving a buildings's energy performance occur early in the design process when basic decisions are made concerning the site, orientation, configuration and passive solar strategies. If the designer does not realize the potential for energy saving during the initial phase the opportunity will be lost to wake significant savings by relatively simple adjustments to the design.

5) Different aspects have to consider in our approach for desert development such as energy and cost efficient architecture, renewable energy systems, waste management, and finally environmentally appropriate technologies.

Acknowledgement

The author would like to thank prof. F. Hammad, chairman of AEA,Cairo and Mr. D. Nentwich, director of KFA, Germany for their help, continual encouragement, and support during various stages of the project.

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Determination of Radioisotopes in Environmental Samples

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1. Introduction

Radioisotopes in the environment effect a radiation exposure of human populations. Besides of the major naturally occuring radionuclides, which includes the isotopes of uranium and thorium plus their daughters and ^{40}K, ionizing radiation from man-made sources in the environment, e.g., worldwide or local fallout from nuclear weapon tests, radionuclides emitted from nuclear facilities under normal or accidential conditions, and radionuclides utilized in consumer or medical applications, contribute to radiation exposure. In connection with the estimation and the valuation of this exposure, the analysis of relevant radionuclides in the biosphere is of fundamental importance.

2. Radionuclides of interest

The major source of radiation exposure is from natural radiation and radioactivity /1-6/. In the norm the principle natural radiation exposure is due to the inhalation of ^{222}Rn decay products, accounting for about 85 % of the total /7/. The remaining 15 % are more or less equally divided between cosmic and terrestrial sources and internally deposited radionuclides. The total radiation dose of the internally deposited radionuclides results mainly of natural occuring radioisotopes: $^{210}Pb/^{210}Po$ (50 %), ^{40}K (30 %), $^{228}Ra/^{224}Ra$ (7 %), and ^{226}Ra (6 %).The radioactice decay properties of the most important radionuclides of the ^{238}U and ^{232}Th series are summarized in Table 1 /2/.

The radiation exposure from man-made sources is very low compared to the human exposure from natural radioisotopes, if accidental situations are not considered. Although several hundred radionuclides are produced by nuclear explosions or are present in irradiated reactor fuel, only a limited number of them contribute significantly to human exposure. These include fission products and activation products, which are created in nuclear reactors and other nuclear devices by the reactions of neutrons with fuel and construction materials. Table 2 gives a survey of those fission and activation products which may be of concern in human exposure /8/. In case of accidental releases, the spectrum of radionuclides could be somewhat different. A compilation of radionuclides which would be of concern during varying periods of time after a nuclear accident are given in /8/ considering four different nuclear accident scenarios.

Table 1: Radioactive decay properties of relevant radionuclides of the ^{238}U and ^{232}Th series

	Nuclide	Half-life	Major decay	Radiation energy in MeV
U-238 series	U-238	4.51 E 09 y	α	4.15 (25%), 4,20 (75%)
	U-234	2.47 E 05 y	α	4.72 (28%), 4.77 (72%)
	Th-230	8.0 E 04 y	α	4.62 (24%) , 4.68 (76%)
	Ra-226	1602 y	α	4.60 (6%), 4.78 (95%)
	Rn-222	3.823 d	α	5.49 (100%)
	Pb-210	21 y	β	0.016 (85%), 0.061 (15%)
	Po-210	138.4 d	α	5.305 (100%)
Th-232 series	Th-232	1.41 E 10 y	α	3.95 (24%), 4.01 (76%)
	Ra-228	5.8 y	β	0.055 (100%)
	Th-228	1.910 y	α	5.34 (28%), 5.43 (71%)
	Ra-224	3.64 d	α	5.45 (6%), 5.68 (94%)

3. Collection and preparation of environmental samples

There are two ways of intake of radionuclides by the public: inhalation and ingestion. To estimate the intake of a radionuclide it is necessary to collect and analyze samples of aerosols, diet or dietary constituents and drinking water. If information about the contamination of the environment with a radionuclide is required, environmental materials which are part of the immediate pathways leading to food and in the end to man must be taken and analyzed. Regarding the terrestrial pathway, samples of soil, vegetation, milk and meat must be considered, for the aquatic pathway, samples of sediment, surface water, water plants and fish have to be taken into account. Sampling principles and sample handling for a variety of matrices have been reported in literature /8,9/. As the concentrations of radionuclides in the environment are normally very low, large quantities of samples are required for radiochemical analysis. Appropriate sized water samples are in the range of 10 to 50 l, for soil and sediment samples up to 1 kg fresh material is sufficient. In case of organic material the collected sample should be of such a size that after drying and ashing at least 20 g of ash are obtained. This means that from a vegetable with high content of water and organic material, e.g. tomatoes, about 3 kg of fresh sample has to be collected.

Before radiation measurements or radiochemical separation should be performed, it is advisable to dry and homogenize the sample materials. Drying reduces the weight and volume of the samples, and the concentrations of the radionuclides of interest are increased. Samples may be dried at room temperature or in a low temperature oven at 105-110 °C without a significant loss of any radionuclide except radioiodine. Samples should be dried for a sufficient period of time at a fixed temperature to acquire a constant dry weight. It is important to avoid contamination during the drying procedure. For this reason it is recommended that samples with high activity levels are processed in a separate area from low level samples.

Table 2: Man-made radioisotopes which may contribute to human exposure /8/

	Nuclide	Half-Live	Fission yield in %	Major decay
Fission Products	Sr-89	50.5 d	4.77	β^-
	Sr-90, Y-90	28.7 a, 64.1 h	5.76	β^-, β^-
	Zr-95, Nb-95	64.09 d, 35.0 d	6.51	$\beta^-\gamma$, $\beta^-\gamma$
	Mo-9, Tc-99m	2.747 d, 6.006 h	6.09	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-103, Rh-103m	39.272 d, 56.116 min	3.03	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-106, Rh-106	372.6 d, 29.92 s	0.4	β^-, $\beta^-\gamma$
	Te-129m	33.6 d	0.661	$\beta^-\gamma$
	I-131	8.021 d	2.875	$\beta^-\gamma$
	Te-132, I-132	76.856 h, 2.3 h	4.282	$\beta^-\gamma$, $\beta^-\gamma$
	Cs-137, Ba-137m	30.0 a, 2.55 min	6.136	β^-, γ
	Ba-140, La-140	12.751 d, 1.6779 d	6.134	$\beta^-\gamma$, $\beta^-\gamma$
	Ce-144, Pr-144	284.45 d, 17.28 d	5.443	$\beta^-\gamma$, $\beta^-\gamma$
Activation products	H-3	12.35 a		β^-
	C-14	5730 a		β^-
	Fe-55	2.75 a		EC
	Fe-59	44.53 d		β^-, γ
	Mn-54	312.5 d		EC, γ
	Co-60	5.27 a		β^-, γ
	Zn-65	243.9 d		EC, γ
	Cs-134	754.2 d		β^-, γ
	Np-239	2.355 d		β^-, γ
	Pu-241, Am-241	14.35 a, 432.0 a		β^-, $\alpha\gamma$
	Cm-242	162.94 d		α
	Pu-238	87.7 a		α
	Pu-239	2.411 E 04 a		α
	Pu-240	6.563 E 03 a		α
	Pu-242	3.735 E 05 a		α

Liquid samples are concentrated by evaporation in the presence of either nitric or hydrochloric acid. Some radionuclides, such as radioiodine, tritium and radioruthenium, may be lost during the evaporation process. For these radionuclides special procedures have to be applied.

Whenever radiochemical separation procedures have to be applied, e.g. for the determination of radiostrontium or α-emitting radionuclides, the sample material must be free of organic carbon. This means that ashing of the samples prior to analysis has to be performed. Carrier elements and radioisotope tracers should be added before ashing. Dry ashing should be used only for those radionuclides which are not volatile at the ashing temperature of at least 450 °C. If samples are not completely dry at the start of ashing, an initial drying step at 105-110 °C should be introduced. The ashing time depends on type and quantity of the sample material. Large samples may require up to 24 hours, and if they are rich in organic material, a second ashing after treatment with concentrated nitric acid may be advisable. Samples which have to be analyzed for volatile elements, e.g.

radioiodine, radioruthenium, radiocesium, ^{210}Pb or ^{210}Po, are prepared for analysis by wet ashing in mineral acids.

After drying and/or ashing samples are usually homogenized using "V" blenders, mixerblenders, ball mills, or others. Homogenizing is extremly important, when subsamples are to be used for analyses. Subsamples of sufficient size should be taken to make shure that they are really representative for the whole material to be analyzed.

4. Determination of radioisotopes

Quantitative measurement of a radioisotope in environmental samples means that extremly small quantities of this nuclide, very often in the range between fg and pg, should be measured in large sample volumes using radiometric detection methods. The mode of decay and the chemical and physical properties of the different radioisotopes to be determined appoint the procedures which have to be applied for the determination.

Gamma emitters can be measured directly in the original sample without the need for chemical separations by gamma ray spectrometry which allows the qualitative identification as well as the quantitative determination in a large variety of samples. It is beyond the scope of this paper to summarize the principles of gamma ray spectrometry and to discuss specific recommendations for the effective and accurate use of this method for environmental samples.

For the determination of an alpha- or beta-emitter it is necessary to separate the radioisotope which should be determined in a first step from the sample material and in a second step from other alpha- or beta-emitters which could falsify the measurement by their radiation. Chemical separation steps are used which are common in classical analytical chemistry methodology, like precipitation, ion exchange, liquid ion exchange, solvent extraction, electrodeposition and spontaneous deposition. Many different procedures for the determination of each radionuclide of interest in various sample materials have been developed during the last four decades and are available in literature. The methods described in the following are used in our laboratories since many years. They have been proved very carefully and give reproducible and reliable results.

4.1 Analysis of tritium /8,10-14/

Tritium present in the environment is both natural and man-made origin. As a result of nuclear weapons testing in the atmosphere, emissions from nuclear installations, and the application and processing of radioisotopes, significant amounts of tritium are released to the environment. In nature, tritium mostly occurs as tritiated water, HTO.

For determination of HTO in water samples, aliquots of the samples are distilled to remove non-volatile quenching materials and non-volatile radioactive substances. Prior to distillation, sodium carbonate (Na_2CO_3) and sodium thiosulphate ($Na_2S_2O_3$) or sodiumsulfite (Na_2SO_3) are added to the sample. The majority of constituents which might interfere remain in the residue together with any radioactive iodide and bicarbonate. An aliquot of the distillate is mixed in a 20 ml polyethylene counting vial with a scintillation

solution /15,16/. The mixture is cooled and counted in a liquid scintillation spectrometer (coincidence type). Without preconcentration, the lower limit of detection (LLD) is in the range of 20-50 Bq/L (counting time 100 min). The LLD can be reduced at least by a factor of 10 by using liquid scintillator counters with very low background which have been developed especially for low-level counting. Electrolytic enrichment of tritium is another possibility to lower the LLD /11/.

For the determination of tritium in tissue water of organic materal, the water is separated by freeze drying and measured as described. Organically bound tritium in the dry residue can be determined by oxidative digestion of the organic material and measurement of the produced water. Samples with higher tritium content are burned in oxigene atmosphere /9,17/, samples with low tritium content are digested by application of the oxidizing plasma technique /18,19/.

4.2 Radiochemical analysis of strontium

A large number of sensitive and reliable procedures for the determination of radiostrontium in various environmental samples are available in literature. Most of them allow the determination of both radioisotopes, ^{89}Sr and ^{90}Sr, whereas others are restricted to the determination of ^{90}Sr only. The latter ones can be used, if the environmental level of ^{90}Sr from old fallout is investigated and no sources for ^{89}Sr input have to be considered. In fresh fallout situations and for emission and immission control of nuclear installations, the concentrations of both isotopes have to be measured.

The procedure which we use in our laboratories for more then 20 years differs only in some not relevant details from those recommended in literature /8,9,12,14,20/. With some modifications in the preparation steps prior to analysis, this method can be applied to all

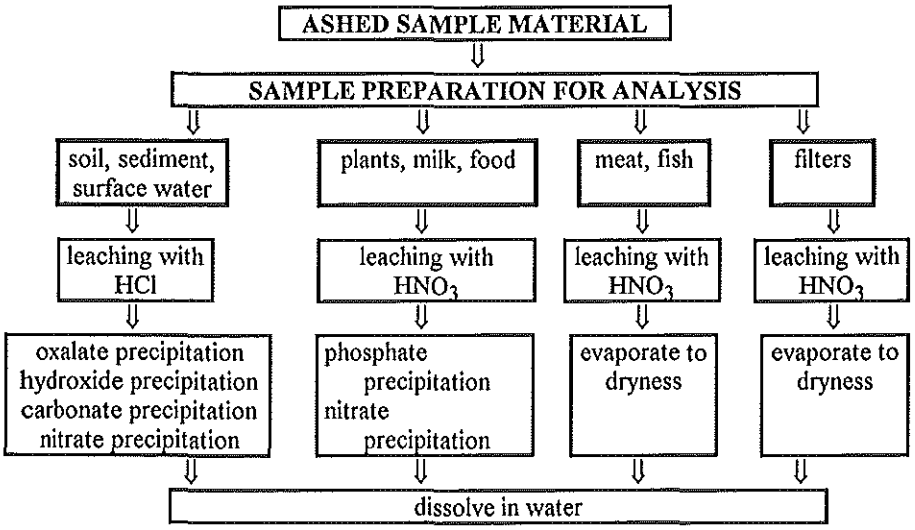

Fig. 1: Preparation of different sample materials for radiostrontium analysis

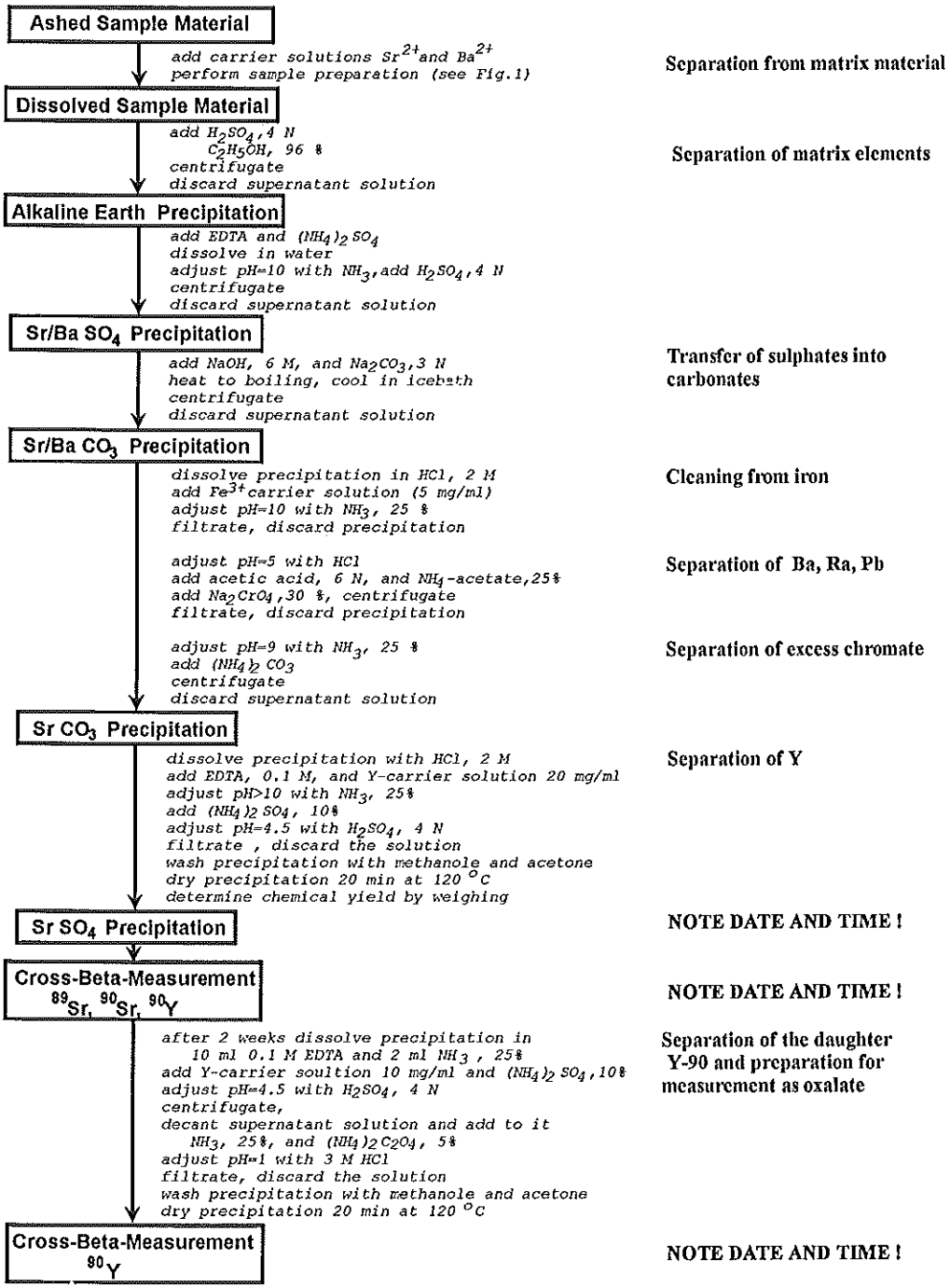

Fig. 2: Scheme of radiostrontium determination in environmental samples

kind of environmental samples and food. Drinking water and ground water which contain very low amounts of matrix elements can be taken for analysis without any further preparations. For all other samples, pretreatment of the material prior to analysis has to be performed in order to separate strontium isotopes from most of the matrix elements, especially from calcium. The most commonly used method for Sr/Ca-separation is the nitrate precipitation of Sr from fuming nitric acid, which is difficult to perform, but gives reliable results. Fig.1 summarizes sample preparations for analysis of various sample materials. In Fig.2 a scheme of the analytical procedure is given. The dissolved sample is cleaned from matrix elements remained, especially iron. Then Sr is separated from Ba, Ra, and Pb. After separation from the daughter ^{90}Y, Sr is precipitated as sulphate and the β^- radiation is measured in a low level proportional counter. After 2-3 weeks the sulphate precipitate is redissolved and the ingrown daugther ^{90}Y is separated from Sr, precipitated as oxalate and measured in a low level proportional counter. The concentration of ^{90}Sr is calculated from the ^{90}Y content of the measured yttrium oxalate precipitate. ^{89}Sr activity is calculated by subtracting the ^{90}Sr activity from the total activity measured in the strontium sulphate precipitate. The lower limit of detection on a 95% confidence level is in the range of 0.009 Bq/sample for ^{89}Sr and 0.006 Bq/sample for ^{90}Sr (chemical yield 80 %, measuring time 1,000 min, background of the ß-counter 0.5 cpm, counting efficiency 40 %). In comparison with the large sample volumes which can be taken for analysis it derives that radiostrontium can be determined very sensitive although the procedure is very time consuming and difficult to handle.

4.3 Radiochemical analysis of ^{210}Pb /9, 12, 14, 21-24/

The procedure described allows the determination of ^{210}Pb in all environmental samples. Drinking water and ground water samples may be taken for radiochemical analysis directly after evaporation without ashing. All other sample materials have to be dried and ashed very carefully, whereby dry or wet ashing can be used. The texture of soil and sediment samples has to be decomposed by aid of fluorine acid in combination with other mineral acids, normally perchloric and nitric acid.

Aliquots of the ashed material (5 g in case of soil and up to 20 g of ashed biological material) are taken for the radiochemical analysis, which is schematically shown in Fig. 3. After addition of Pb^{2+}-carrier solution as chemical yield tracer, lead is leached out of the sample material with 3 M HBr as tetrabromo-complex and is detached from the matrix elements by extraction with trioctylamine/toluene. After backextraction with concentrated HCl, traces of Bi are separated by precipitation as BiOCl. Finally, Pb is precipitated as $PbCrO_4$. The precipitate is distributed on a filter paper as uniform as possible. After 8-10 days, the precipitate is covered with a filter paper of equal size and specification (7-9 mg/cm^2) and the beta radiation is measured in a low level proportional counter. Only the high energy beta radiation of the daughter ^{210}Bi is measured in this way, because the covering filter paper absorbs the low energy beta radiation of ^{210}Pb and the alpha radiation of ^{210}Po, daughter product of ^{210}Bi. The concentration of ^{210}Pb is calculated from the ingrown ^{210}Bi. The lower limit of detection (95 % confidence level) is in the range of 0.006 Bq/sample (measuring time 1000 min, chemical yield 80 %, counting efficiency 40 %). Due to the large sample quantities which can be processed, very low activity concentrations of ^{210}Pb can be measured in environmental samples.

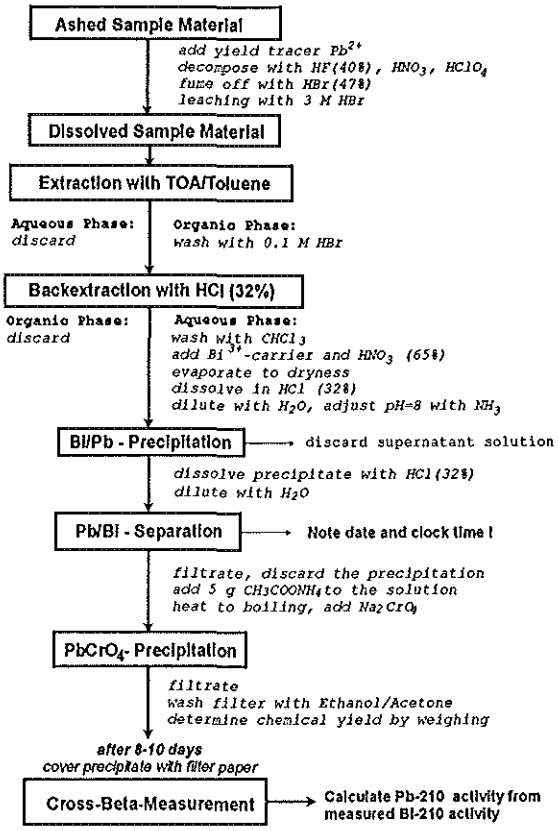

Fig. 3: Scheme of the procedure for ^{210}Pb determination in environmental samples

4.4 Radiochemical analysis of ^{210}Po /9, 12, 14, 22, 24-26/

The chemical behavior of polonium shows 2 peculiarities: compounds are much more volatile than compounds of metal ions with a comparable chemistry, and polonium is the only element that spontaneously deposites on nickel, copper, silver, gold or platinium from dilute HCl solution /25/. Both peculiarities are considered in the determination procedure, which is shown schematically in Fig. 4.

To prevent severe losses of polonium during drying and ashing of the sample materials, special procedures have to be applied. Samples may be dried at room temperature or by freeze drying. Ashing should be performed using oxidizing plasma technique /18,19/ or by wet ashing procedures /26/. ^{208}Po is added to the sample as internal yield tracer before ashing. Polonium is leached out of the ash with HCl, separated from matrix elements as well as soluble trace elements by coprecipitation with Te. Then polonium is disolved in dilute HCl and deposited on silver platelets. The alpha activities of ^{208}Po and ^{210}Po are measured using surface barrier detectors. For a measuring time of 1000 min and a chemical yield of 60 %, the lower limit of detection is in the range of 0.01 Bq/sample.

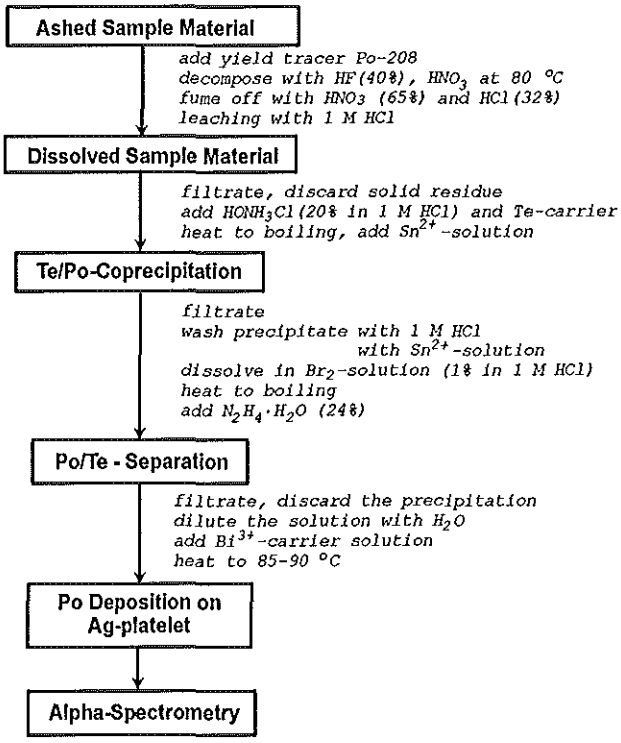

Fig. 4: Schematic representation of the analytical procedure for the determination of ^{210}Po in environmental samples

4.5 Detection of Radon Gas

As already mentioned above, inhalation of ^{222}Rn decay products is the main source of radiation exposure from natural radiation and radioactivity. For this reason properties and behavior of radon and thoron and their short living decay products in air have been subject of many research programs and a substantial knowledge is available today /2, 27-29/. More details of this field are given in another lecture of this seminar by E. Piesch, entitled "Determination of Radon and Radon Daughters in Air".

Within the food chain, ^{222}Rn concentrations are normally very low and without any importance because of the rapid elimination of ^{222}Rn from the body. Only in drinking water, especially if it is of deep groundwater origin, higher ^{222}Rn concentrations have been detected, which contribute to the ingestion dose of the population living in these regions /2/ and which are a significant source of ^{222}Rn in dwellings as a result of degassing from tap water. The measurement of the ^{222}Rn concentration in water can be relativly simple performed by liquid scintillation counting procedures in a low-level liquid scintillation spectrometer which allows α/β-pulse-shape discrimination and by this alpha spectrometric measurements /30-34/. For a counting time of 60 min and a sample volume of 10 ml, the lower limit of detection is about 0.1 Bq/l.

4.6 Radiochemical analysis of ^{226}Ra

Among the natural occuring radium isotops, ^{226}Ra is the most important from radio-ecological point of view. ^{226}Ra is widely distributed in the environment and varies in concentration depending on the geological conditions. For determination of radium, the isolation of radium from the sample material is required. Water samples are evaporated to dryness and ashed if organic material is present in the residue. Biological material is dried at 105-110 °C, afterwards ashed carefully applying dry or wet ashing procedures. Soil and sediment samples are decomposed by aid of fluorine acid in combination with other mineral acids. The ashed sample, or an aliquot of it, is dissolved in 3 M nitric acid after Ba carrier solution has been added for chemical yield determination. Radium is precipitated from acidified citric acid solution together with Ba and Pb as sulphate and separated from Ca, Mg, Th and Po. By redissolving and repeating the precipitation several times the Ba/Pb/Ra precipitate is cleaned. Then the precipitate is dissolved in alkaline EDTA solution and Ra is slowly precipitated with an excess of Ba at pH=4.5, receiving a precipitate in which $RaSO_4$ is completely occluded by $BaSO_4$. After three weeks, when the daughters ^{222}Rn, ^{218}Po, and ^{214}Po are in equilibrium with the ^{226}Ra, total alpha activity is measured in a low level proportional counter. Fig. 5 shows schematically the analytical procedure used /24, 36/, which is comparable to procedures used in other laboratories for the determination of ^{226}Ra /9, 12, 14, 35/. Chemical yields between 60 and 90 % are obtained. The lower limit of detection on a 95 % confidence level is in the range of 0.001 Bq/sample.

If a low level liquid scintillation counter is available, the Ba/Ra-sulphate precipitate may be dissolved in alkaline DTPA solution, transfered to a liquid scintillation vial and mixed with organic scintillant. After sealing the vial, the sample is left until equilibrium of ^{226}Ra and ^{222}Rn is established, before the measurement in the liquid scintillation spectrometer is performed. The lower limit of detection on a 95 % confidence level is in the range of 0.01 Bq/sample /37/.

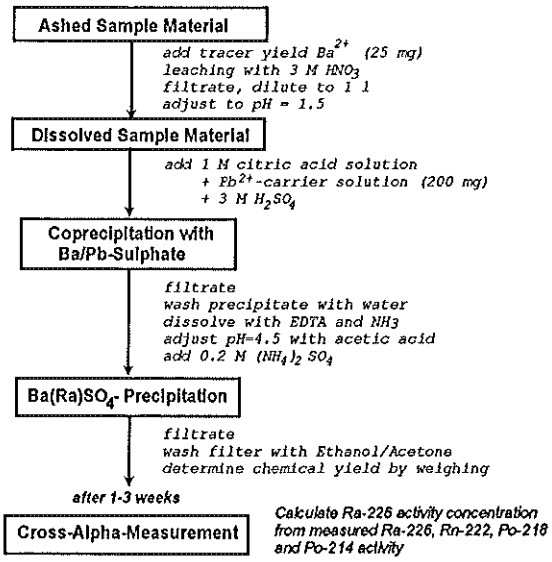

Fig. 5: Scheme of the radiochemical procedure for ^{226}Ra determination

4.7 Radiochemical analysis of thorium and uranium isotopes /9, 12, 14, 24, 38-45/

Thorium and uranium isotopes are determined by applying the isotope dilution analysis. ^{229}Th and ^{232}U are used as tracers for chemical yield corrections, because these isotopes are not present in the environment. A procedure for the radiochemical determination is given in Fig. 6. Thorium and Uranium may be analyzed separately following this procedure, but as there are many identical separation steps for both elements, it is very often of advantage to analyze them simultaneously.

Aliquots of carefully ashed sample materials are taken for analysis. ^{229}Th and ^{232}U are added as tracers. ^{232}U should be cleaned before use by a simple ion exchange procedure from the daughter ^{228}Th , otherwise the ^{228}Th content of the sample has to be corrected arithmetically. Up to 5 g of soil or sediment ash is decomposed by aid of fluorine acid in combination with mineral acids /26, 45/. The residue is leached twice with 8 M nitric acid. Of all other sample materials, up to 20 g of ash may be taken for leaching. U and Th are separated from most of the matrix elements by extraction from the dissolved sample material with TOPO (trioctylphosphine oxide) in cyclohexane. After backextraction with NH_4F in HCl, the U/Th fraction is cleaned by coprecipitation with LaF_3. To receive a complete precipitation of U, Ti(III) was added for reduction of U(VI) to U(IV), which is like Th completely coprecipitated. After redissolving the precipitate with a mixture of boric and nitric acid, U is transfered to U(VI) with H_2O_2. Then U is separated from Th on an anion exchanger column using the different stabilities of chloro- and nitrato-complexes. Whereas Th passes the column with the sample solution, U is adsorbed strongly on the column.

Th is completely washed out of the column with additional 9 M HCl. The solution is evaporated and redissolved in 7.2 M nitric acid. Th is cleaned from boric acid by extraction with TOA (trioctylamine) in toluene and backextraction with diluted HCl. In a last step, Th is electrodeposited from oxalate solution on stainless steel platelets and alpha-spectrometric measurement using surface barrier detectors is performed. The concentrations of ^{228}Th, ^{230}Th, and ^{232}Th are calculated with respect to the recovery of ^{229}Th tracer. The chemical yield is in the range of 40 to 80 %. For a measuring time of 1000 min the lower limit of detection (95 % confidence level) is about 0.001 Bq/sample. In principle, it is also possible to calculate the concentration of ^{227}Th, a daughter of ^{235}U. As the concentrations are very low in environmetal samples (only 1.5 % of total Th), and the ^{227}Th-peak is very broad and disturbed by peaks of other decay products, the results for ^{227}Th-activities are very uncertain.

Uranium is eluted with diluted nitric acid from the column, electroplated on stainless steel platelets from oxalate solution, and measured alpha spectrometrically. The concentrations of ^{234}U, ^{235}U, and ^{238}U are calculated with respect to the recovery of ^{232}U tracer. The chemical yield is in the range of 50 to 80 %. The lower limit of detection (95 % confidence level) for a measuring time of 1000 min is about 0.001 Bq per sample and nuclide.

It should be mentioned that total Th and total U may be determined as heavy elements by severeal methods of analytical chemistry, e. g. fluorimetry, spectrophotometry, neutron activation analysis, and inductive coupled Plasma (ICP)-ion source mass spectrometry. With these methods the long living isotopes are determined which represents the bulk of the masses of uranium and thorium isotopes. If the different isotopes of Th and U have to be quantified individually, the choice of methods is restricted to radiochemical separation procedures followed by alpha spectrometric measurements.

Very often, radium equivalent uranium is measured by means of gamma spectrometry using high purity germanium detectors. The gamma lines of ^{214}Bi and ^{214}Pb are measured and the uranium concentration in the sample is calculated on condition that uranium and all decay products in the sample are in equilibrium. As it is very rare that this assumption is correct, these measurements are only of minor importance.

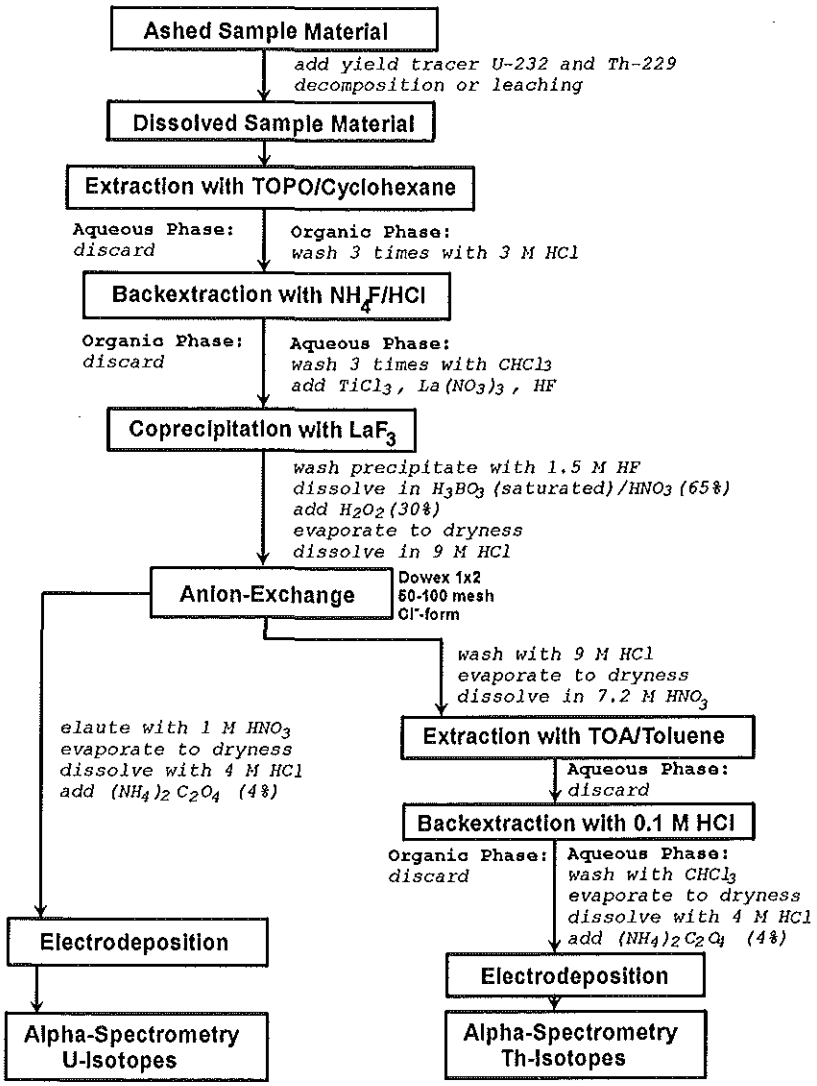

Fig. 6: Scheme of the radiochemical procedure for the determination of thorium and uranium isotopes (if only thorium has to be analyzed, all steps with H_2O_2 and $TiCl_3$ as well as the extraxtion step with TOA/Toluene have not to be performed)

4.8 Radiochemical analysis of plutonium /8, 9, 12, 14, 46-49/

Soil and sediment samples as well as plant, food and organic filter samples are dried at 105-110 °C until their weight remains constant. Water samples are evaporated to dryness. Fish and flesh samples are covered with concentrated nitric acid and carefully fumed off to dryness. The dry sample material is ground and carefully dry ashed at 550 °C. Fiber glass filters are crushed and ashed at 500 °C, this temperature should not be exceeded to avoid melting of the glass fibers.

Up to 100 g of soil ash or up to 20 g of ash of other samples are taken for analysis. ^{236}Pu or ^{242}Pu is added as tracer for the determination of the chemical yield. Then Pu isotopes are leached out of the ashed sample material first with a HNO_3/HF-solution and then with a $HNO_3/Al(NO_3)_3$-solution. Separation of Pu from most of the matrix elements and interfering alpha emitters, like Po, Ra, Am and Cm, is achieved by solvent extraction with 0.2 M TOPO (trioctylphosphine oxide) in cyclohexane. Pu then is backextracted with ascorbinic acid in hydrochloric acid. The Pu fraction is radiochemically cleaned from U, Th, and Np by coprecipitation with LaF_3 and anion exchange. Then Pu is electrodeposited from oxalate solution and measured in an alpha spectrometer.

The concentrations of ^{238}Pu and $^{239+240}Pu$ are calculated with respect to the recovery of ^{236}Pu or ^{242}Pu tracer. In case of ^{239}Pu and ^{240}Pu, the sum of these two nuclides is measured, because ^{239}Pu and ^{240}Pu are not separated in the alpha spectrum, as their alpha energies are very similar and the resolution of alpha spectrometers commonly used are not sufficient to separate them. With the proposed analytical procedure (see scheme in Fig. 7) chemical yields in the range of 70 to 90 % are achieved. The lower limit of detection on a 95 % confidence level for a measuring time of 1000 min is below 0.001 Bq per sample and nuclide.

The same Pu preparation can be used to determine the ^{241}Pu concentration in the sample material, either by direct measuring of the electrodeposited Pu fraction by liquid scintillation counting /50/, or after redissolving the Pu-fraction, extraction of Pu in TOPO/cyclohexane, mixing this organic phase with a suitable scintillant, and measuring with a liquid scintillation counter as well /51/. The lower limit of detection on a 95 % confidence level for this determination is about 0.05 Bq/sample for a measuring time of 100 min. For the direct measurement, the lower limit of detection (95 % confidence level) is about 0.1 Bq/sample for the same experimental conditions.

It should be noticed that the concentration of ^{241}Pu in environmental samples is much higher than that one of the other Pu isotopes. The radiological burden caused by inhalation and ingestion of ^{241}Pu is of minor importance, because of the short half-life time of 14.9 y and the beta-decay with a maximum beta energy of 21 keV. From the radiation protection point of view the daughter product of ^{241}Pu, ^{241}Am, has to be considered, because in the middle of the next century the activity concentration of ^{241}Am will reach its maximum. As the radiotoxicity of the alpha emitter ^{241}Am is much higher than that of the beta emitter ^{241}Pu, and because Am is much more mobile in the biosphere compared to Pu, it is important to keep the ^{241}Pu emissions under control and to monitor the existing ^{241}Pu-concentrations in the environment.

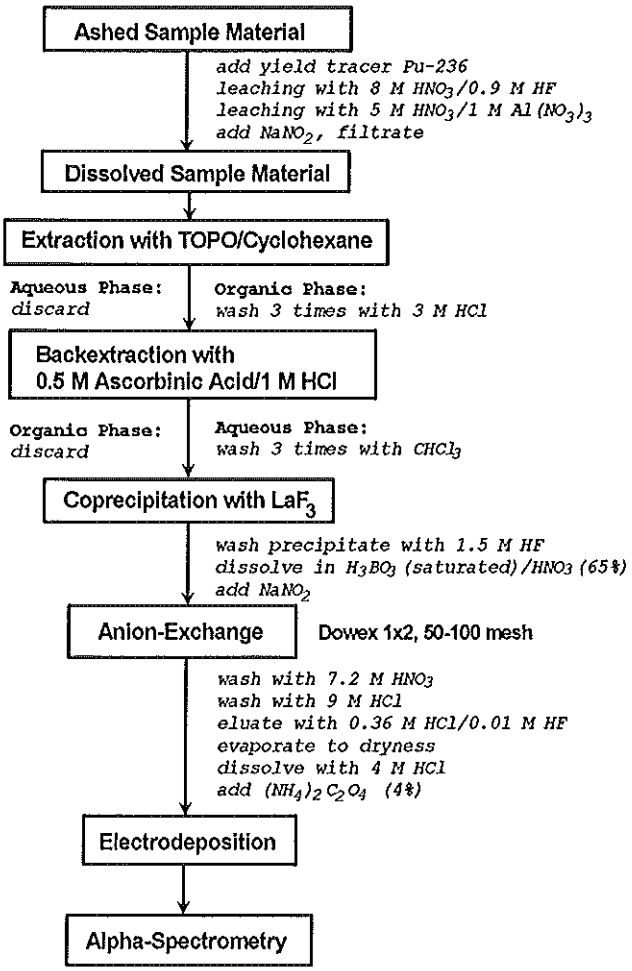

Fig. 7: Schematical representation of the radiochemical procedure for plutonium determination

4.9 Radiochemical analysis of americium and curium /8, 9, 14, 48, 49, 52/

The chemistry of americium is very similar to that of curium. As there is no disturbance of the different alpha emitters of americium, ^{243}Am and ^{241}Am, with the alpha emitters of curium, ^{242}Cm and ^{244}Cm, in the alpha spectrum, there is no need to perform individual procedures for radiochemical determination. ^{243}Am serves as yield monitor for both elements.

After adding of ^{243}Am tracer to the ashed sample material leaching with concentrated mineral acids is performed. Which acids or combination of acids are taken depends on the nuclides to be determined in this leachate. If for example Pu should be determined, leaching is performed with HNO_3/HF- and then with a HNO_3/$Al(NO_3)_3$-solution. By

extraction with TOPO /trioctylphosphinic oxide) in cyclohexane, thorium, uranium and plutonium isotopes are separated and can be determined as already described. The remaining acid solution is brought to pH=1.5 adding carefully NH_3-solution. From this weakly nitric acid solution Am and Cm are extracted by TOPO/cyclohexane, whilst the most important matrix elements Na, K, Mg, Ca, Al, and Fe are left in the acid solution. Extraction may be performed by agitation in a separatory funnel or with an extraction column filled with kieselgur that had been loaded with TOPO/diethyl benzene /52/. Am and Cm are bachextracted with 2 M nitric acid and cleaned by two ion exchange procedures from iron and rare earth elements. Then electrodeposition from oxalate solution is performed and the preparation is subjected to alpha spectrometric measurement. The concentrations of ^{241}Am, ^{242}Cm and ^{244}Cm are calculated from the spectrum with respect to the recovery of ^{243}Am. With the proposed analytical procedure (see scheme in Fig. 8) chemical yields in the range of 40 to 80 % are achieved. The lower limit of detection on a 95 % confidence level for a measuring time of 1000 min is about 0.001 Bq per sample and nuclide.

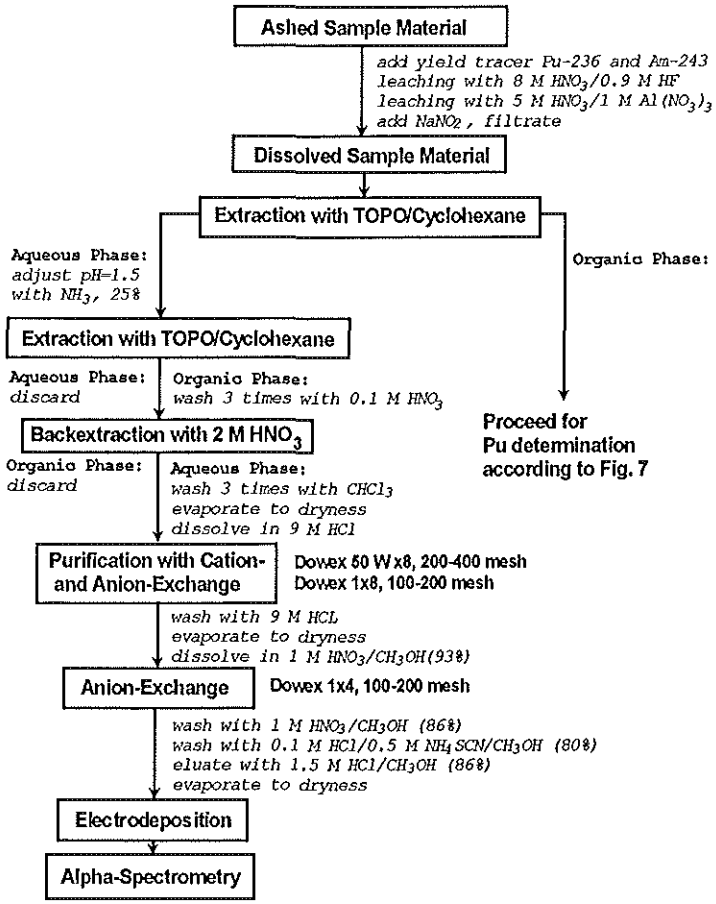

Fig. 8: Schematical representation of the radiochemical procedure for amercium and curium determination

5. Analytical quality control /8/

Quality control measurements are necessary to provide documentation to show that the achieved analytical results are reliable. The reliability of results is a function of precision (reproducibility) and accuracy (true value). The precision of results can easily be determined by internal measurements. The determination of accuracy, however, in most cases requires more detailed procedures. Analysis should be performed by as many different methods, analysts and techniques as possible, and in addidition control analysis with reference materials that are as similar as possible to the materials to be analysed. It is advisable on a routine base to participate in interlaboratory comparisons. Agreement between certified or the most probable mean value and observed value is a direct measure of the accuracy for that particular determination.

Calibrations of measurement systems should be carried out with standards of the radionuclides to be determined. The standards should be accompanied by certificates which specify activity, purity and accuracy. It is important that calibrations are performed with standard samples which have the same chemical composition and the same concentration like the sample to be measured, and that sample geometry and counting configuration is identical to the real sample.

The status of equipment should be checked routinely by measuring background, blanks, and standards. These results often give the first indication of analytical difficulties. Analytical control samples generally constitute about 10-15 % of the total samples.

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MEASUREMENT OF RADIOACTIVITY LEVELS IN SOIL IN THE NILE DELTA AND MIDDLE EGYPT

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Abstract - Concentrations of radionuclides in surface soil across the Nile Delta, the north coast of Egypt, and Middle Egypt have been measured using a hyperpure germanium spectrometer. The concentrations obtained of ^{40}K, the ^{232}Th series, and the ^{226}Ra series are expressed in Bq kg^{-1} of dry weight, and the exposure rates are expressed in nGy h^{-1} of wet weight. The activity concentrations of ^{137}Cs in soil are expressed in Bq m^{-2}.

Introduction :

The work aims to initiate a radiological assesment program for Egypt, for establishing a baseline map of radioactivity background levels in the Egyptian environment. The baseline map will be used as reference information to assess any changes in the radioactivity background level, due to any geological processes or artificial influences on the Egyptian environment.

Sampling and Sample Preparation :

The area under investigation was divided into 18 regions, the Mediterranean coast north, the Delta, the cultivate area of the Nile valley, and Naser lake south. In this work 13 regions were studied.

The region of interest was divided as nearly as possible into squares with each square about 50 km per side. Six to 10 samples were collected from each square. The distance between neighboring samples ranged from 10-20 km. The sampling sites were randomly selected in the cultivated lands of the Nile valley.

The sites were fertilized with phosphate, potassium and other, which contain trace concentrations of uranium.

The collected samples were prepared for gamma activity analysis. Each soil sample was weighed and carefully sealed for 4wk to reach secular equilibrium between ^{226}Ra and ^{232}Th and their respective progeny.

Gamma measurements :

High resolution gamma ray spectrometer, based on coaxial hyperpure germanium detector of a photopeak relative efficiency of about 30% and an energy resolution of 1.95 keV FWHM for the 1.332 keV gamma transition of ^{60}Co, was used for the gamma spectrometry of the soil samples.

The activity of ^{214}Bi and ^{214}Pb in equilibrium with their parents was assumed to represent the ^{238}U activity, while the activity of ^{228}Ac was assumed to represent the ^{232}Th activity.

The ^{238}U series concentrations were determined from the energies 351.9 keV (^{214}Pb), 609.3 keV (^{214}Bi), 768.4keV(^{214}Bi) 1,120.3keV(^{214}Bi), 1,238.1 keV, and 1,764.5 keV (^{214}Bi).

The ^{232}Th series concentrations were determined from the energies 338.4 keV (^{228}Ac), 583.1 keV (^{208}Tl), 911.1 keV (^{228}Ac), 968.9 keV (^{228}Ac), and 974.7 keV (^{228}Ac).

The concentrations of ^{40}K were determined from the 1460 keV gamma energy and the ^{137}Cs concentrations were determined from the 661.66 keV gamma transition.

Results and conclusions :

The dry weight activity concentration are for ^{40}K, the ^{238}U series, and the ^{232}Th-series in Bq/kg and for ^{137}Cs in Bq/m^2 were determined for 162 soil samples from 13 regions.

Also the absorbed dose rates in air nGy/h, calculated for a height of 1m above the ground surface for each location for the wet weight concentrations of the natural nuclides.

The type of soil is classified as sandy, clay or loamy soil due to the mechanical analysis.

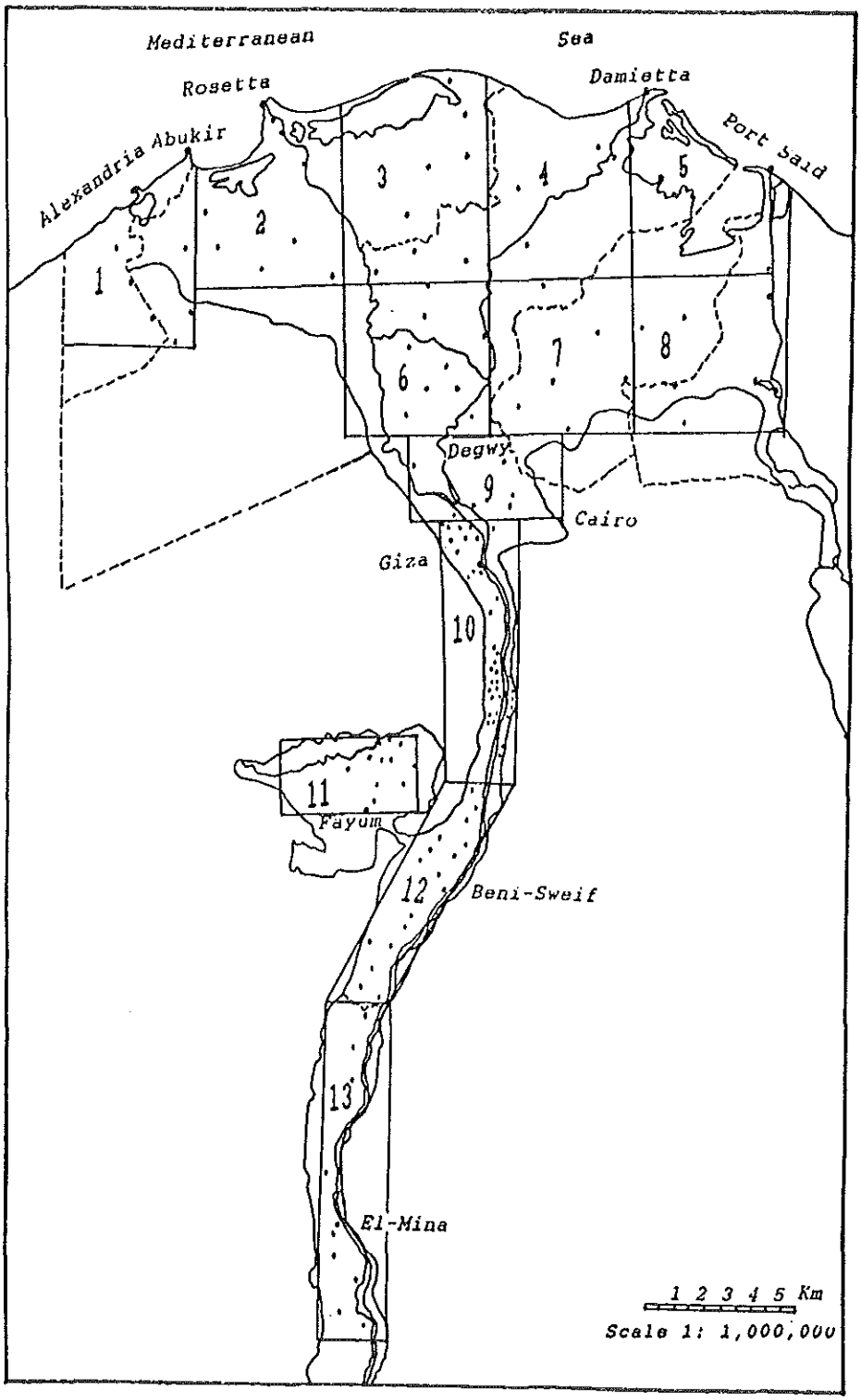
^{40}K concentrations in Bq/kg for dry weight ranged from 29, for sandy soil in the western desert, to 653, for the loamy soil at Degwy.

^{238}U series values ranged in Bq/kg for dry weight, from 2.5 for sandy soil, to 95.6 for black coastal sand at Rosetta.

The absorbed dose rate calculated for a height of 1m above ground surface for each location calculated for the wet weight concentrations of the natural radionuclides, were measured. It's value in nGy/h ranged from 7.6 for sandy soil in region 8, to 93.2 for the coastal sand at Rosetta.

The ^{137}Cs values in Bq/m^2, ranged from 38 for sandy soil at region 1, to 2,644 at Damietta for clay.

The measurements were started in 1989,3 years after the Chernobyl accident also the ^{134}Cs concentrations were less than the lower limit of detection of the Hp Ge detector used. So the percentage of the ^{137}Cs from the Chernabyl accident can'nt be defined accurately.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URANIUM CONCENTRATIONS IN SEDIMENTS OF THE SUEZ CANAL

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ABSTRACT

Suez canal botton sediment samples have been analyzed for uranium. The method is based on the extraction of uranium with trioctylphosphine oxide/cyclohexane (TOPO), followed by reextraction and separation on anion exchange resins, and finally electrodeposition. The α-activities of ^{238}U and ^{234}U were measured with surface barrier detectors and concentrations in Bq/kg dry weight were calculated. The obtained results were compared with concentrations determined by gamma spectrometric measurements. The data point to a state of disequilibrium between ^{238}U and RaeU (radium equivalent uranium), which is attributed to the escape of radon.

INTRODUCTION

The baseline natural radioactivity in the Suez Canal has recently been measured by gamma measurements using HpGe detectors [Ref. 1,2]. The ^{214}Bi and ^{214}Pb in equilibrium with their parents were assumed to represent the ^{238}U activity.

The decay series arising from ^{238}U contain radioactive isotopes of many different elements. These daughters of uranium may be separated from their parents and from each other in the course of normal geological processes such as chemical weathering and precipitation of minerals from aqueous solutions by biological and inorganic processes. Such processes break the radioactive decay chains because of the differences in geochemical properties of the daughters of uranium [Ref. 3].

^{234}U is produced from ^{238}U by the follwing series of decays:

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta} {}^{234}Pa \xrightarrow{\beta} {}^{234}U.$$

If secular equilibrium has been established, the activity of ^{234}U is equal to that of ^{238}U. This equilibrium may be desturbed because of the difference in geochemical behavior of U and Th.

Uranium occurs on the surface of the Earth in oxidizing environments as uranyl ion UO_2^{2+}, most probably as complexes such as $(UO_2)(CO_3)_3^{4-}$ [Ref. 3]. Wheras thorium remains in the tetravalent state and is rapidly removed from sea water by adsorption on the surface of solids, uranium is concentrated in the aqueous phase. This difference in behavior of U and Th leads to different activity ratios of the $^{234}U/^{238}U$ in sediment samples from different sampling locations.

The present work aims to study the equilibrium between ^{238}U and it's respective progeny by the comparison of the concentrations of ^{238}U and ^{234}U using α-spectrometry as well as products of ^{238}U decay series using gamma spectrometry.

EXPERIMENTAL METHODS

Preparation of Uranium for α-spectrometry

Procedures for alpha spectroscopic measurements can be subdevided into five steps [Ref. 4]:

(i) Sampling,
(ii) Sample pretreatment, dissolution or leaching,
(iii) Chemical separation,
(iv) Source preparation,
(v) Alpha spectrometry.

The 1st step is discussed in detail in [Ref. 1], while the 2nd, 3rd, and 4th steps, which deal with chemical procedures, are discussed in detail in [Ref. 4].

For total uranium determination in soil or sediment samples, 2 to 5 grams of the sample ash is weighed into a Teflon beaker or a Pt-crucible, then treated with nitric-hydrofluoric acid mixture 1:1 and fumed off to complete dryness. The residue is dissolved in 8M HNO_3 [Ref. 5], and ^{232}U tracer is added for chemical

yield determination. 2 ml H_2O_2 are added and the solution is heated to boiling to ensure that all dissolved uranium is present in the hexavalent state.

TOPO is used as an extracting agent [Ref. 6, 7]. The partition coefficient reaches its maximum beetween 5M and 8M HNO_3. All matrix elements, such as Na, K, Mg, Ca, Al and Fe, are not extracted by TOPO and are removed, while Pu, Np, U and Th are extracted in the TOPO phase. The TOPO phase is washed with 3M HCl to wash out the residual HNO_3, which could disturb the re-extraction.

Uranium is back extracted with 1M NH_4F/ 0.1 M HCl to the aqueous phase which is washed with CCl_4 or CHCl3. Uranium obtained in the hydrochloric solution is reduced to U (IV) by $TiCl_3$, then copercipitated with LaF_3 after adding La $(NO_3)_3$ 25 mg/ml and HF 40 %. The solution then is centrifuged, the precipitate is dissolved in saturated hot boric acid and concentrated HNO_3. H_2O_2 is added, which transfers uranium to U (VI), then the solution is evaporated to dryness. The residue is dissoved in 9M HCl [Ref. 7].

The sample solution is loaded onto a conditioned anion exchange column and passes through by gravity flow (about 0.5-1ml/min). Dowex 1X2, 50-100 mesh, is used, which is a strongly basic gel type polystrene resin with appropriate functional groups. U(VI) is separated from thorium and plutonium using the different stabilities of chloro-and nitrato-complexes.

After washing out thorium with 9M HCL, 1M HNO_3 is used for the eluation of uranium.

The elute is evaporated to dryness in a crystallizing dish and fumed off with concentrated HCl.

Electrodeposition from oxalate-solution on stainless steel was performed, which has been proved to be the most efficient and statisfactory procedure [Ref. 6, 7].

Alpha Spectrometry

Silicon surface barrier detectors were used for measurements, because of their excellent resolution, high permissible counting rate, low background, and excellent stability. Also there is no significant variation of the detector efficiency in the energy interval 2.5 MeV to 8.8 MeV. This makes the quantitative evaluation of α-particle spectra much simpler than in the case of gamma ray spectra [Ref. 8].

The counting time is 1000 minutes. From the uranium alpha spectrum the concentrations of ^{238}U, ^{234}U, as well as ^{235}U, can be calçulated.

RESULTS AND DISCUSSION

The table gives the concentrations of ^{238}U and ^{234}U in sediment samples of the Suez Canal in Bq/kg dry weight obtained by radiochemical analysis and alpha-spectrometric measurements. The concentrations of equivalent U are determined by gamma spectrometry using HpGe detectors [Ref. 1] in Bq/kg dry weight. Each value is an average of five measurements obtained from the gamma energies 351.9 keV (^{214}Pb), 609.3 keV (^{214}Bi), 768.4 keV (^{214}Bi), 1,120.3 keV (^{214}Bi), 1,238.1 keV (^{214}Bi) and 1,764.5 keV (^{214}Bi).

The studied sediment samples were taken from different sites in the Suez Canal: from Port Said (at the Mediterranean) Lake Temsah, Bitter lake and Suez gulf.

With the exception of one sample collected from Gulf of Suez (No. 37), the data indicate very close values for ^{238}U and ^{234}U within the reported experimental errors, thus suggesting maintainance of equilibrium between the two isotopes. On the other hand, the data indicate wide deviation from the equality ratio between ^{234}U and RaeU, which suggests a disturbance for the state of equlibrium in these sediments. Such disequilibrium may be attributed to:

1- Escape of radon because of its gaseous nature. This leads to lower concentrations of all the post-radon isotopes in the decay series, and hence to lover RaeU values.

2 Selective deposition of ^{230}Th or ^{226}Ra or both, having lower solubilities in water than U. However this would cause an increase in the RaeU content of sediments which is the reverse of the presented results.

Therefore the first possibility is favored. However, a substantially larger number of samples is needed to reach more reliable and sound conclusions.

Comparison of uranium concentrations in Bq/kg dry weight, obtained with alpha and gamma spectrometric measurements in sediment samples from Suez Canal

origin of sediment sample	alpha spectrometry		gamma spectrometry
	U-238	U-234	U-Series
Port Said 5	16.05 ± 5.9	20.2 ± 4.0	14.5 ± 0.7
Port Said 12	10.1 ± 3.0	10.1 ± 1.5	9.8 ± 0.5
Lake Temsah*	27.4 ± 5.6	24.2 ± 5.7	9.4 ± 0.5
Bitter lake 26	57.5 ± 14.2	56.7 ± 1.4	12.4 ± 0.4
Bitter lake 28	12.6 ± 3.0	16.7 ± 3.1	9.8 ± 0.3
Suez 37	57.4 ± 1.1	29.7 ± 7.5	8.6 ± 0.5
Suez 44	30.4 ± 3.8	33.6 ± 3.5	15.2 ± 1.0

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Determination of Radon and Radon Daughters in Air

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Abstract

The radon dose from inhaled Rn and short-lived Rn daughters is the dominant component of natural radiation exposure of the general population. The paper provides an overview of the behaviour of Rn and short-lived Rn daughters in air, the measurement techniques and the relevant problems of Rn measurement. Aspects of the indoor Rn exposure are discussed as well as reference levels of the Rn concentration in air which have been recently recommended for the public and workplaces.

1 Introduction

Radon is a radioactive, inert gas which is about ten times heavier than air. With an extremly low concentration in air ($1:10^{20}$) radon is nevertheless the natural radionuclide of highest interest. Not radon directly, but radon daughters are the dominant components of the radon exposure. Radon is formed in the ground by the radioactive decay of radium and is present in relatively high concentrations in soil air and water. Due to the longest half life of 3.8 days mainly ^{222}Rn can reach the atmosphere. In the indoor environment the short-lived Rn decay products are attached to aerosol particles or plated out on wall surfaces. In areas with a higher uranium contribution in the ground extremly high Rn concentrations can be found.

The relatively high rate of lung cancer among underground miners has long been investigated and the first epidemiological studies have been available at the end-1960s. Since the late 1970s the importance of indoor Rn as a potential risk for the general public has been finally recognized. In the meantime thousands of houses and other buildings worldwide have been tested for evaluated levels of Rn.

2 Characteristics of Radon and its decay products

^{222}Rn, formed in the uranium decay chain from decay of ^{226}Ra (Fig. 1), is the most important radon isotope because of its longest half life of 3.8 days. In contrast to ^{220}Rn (55 s) and ^{219}Rn (4 s), ^{222}Rn can reach the outdoor atmosphere, when formed within about 1 m of the earth surface, and the indoor environment, when formed in

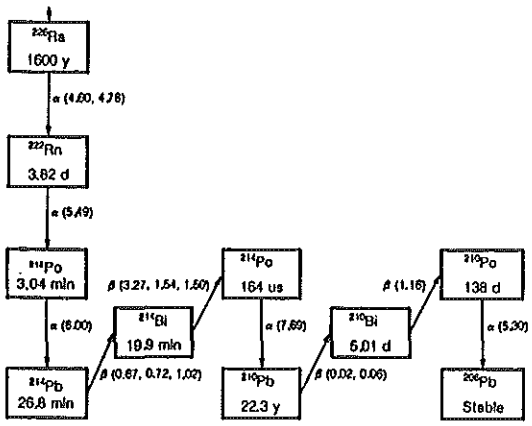

Fig. 1 ^{226}Radon decay chain

the ground or in the building material. Radon decays to radionuclides that are chemically active and relatively short-lived with half lifes of less than 30 minutes. If inhaled and collected in the lung they are likely to decay to ^{210}Pb before removel by lung clearence mechanism. Mainly the α-radiation from the polonium isotopes ^{218}Po (6 MeV) and ^{214}Po (7.69 MeV) contributes to the radiologically significant lung dose to which increased risk of lung cancer is attributed.

In the indoor environment (Fig. 2) the decay of Rn daughters results in ions of heavy metal which react with vapor of H_20, $N0_2$ and other spurious gas forming stable clusters (diameter 0.5 to 3 nm)(unattached decay products). Free ions and these clusters are attached to aerosol particles (diameter 0.01 and 1 μm) (attached decay products) or plated out on indoor surfaces. The complex behaviour of decay products depends on the chemical reactivity, the aerosol particle concentration and size, the plate out and deposition on indoor surfaces. The behaviour of Rn daughters in air is thus correlated with that of the aerosol particles which change frequently in the concentration due to the ventilation rate, the deposition rate and the human behaviour (aerosol production by cigarette smoke, for instance).

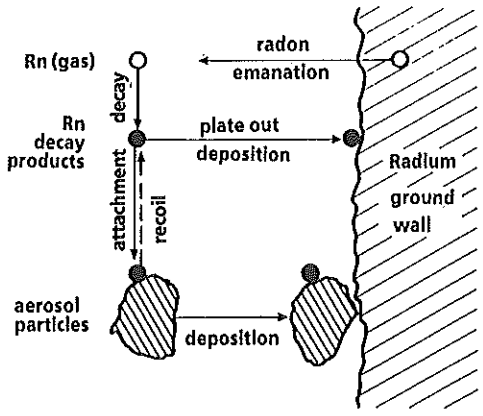

Fig. 2 Radon decay product removal mechanism in the indoor environment

3 Determination of the radon exposure

As the consequence of the different behaviour of Rn and Rn daughters, there is no radioactive equilibrium between radon and its short-lived decay products. In fact, mainly Rn daughters and only to a small extent radon gas itself contributes to the lung dose. Consequently both contributions have to be measured separatly. In practise, however, long-term integrated measurements of the Rn concentration are favoured because only these measurements are representative for the estimation of radon exposure (Fig.3).

In order to describe the risk of radon exposure it is necessary to estimate the so-called equilibrium-equivalent radon concentration C_{eRn} of the relevant short-lived Rn daughters in air. The value of C_{eRn} is measured directly or is calculated from the measured Rn concentration C_{Rn} using the actual value of the so called equilibrium factor F.

$$C_{eRn} = F \cdot C_{Rn} = 0.105 \cdot C_1 + 0.516 \cdot C_2 + 0.379 \cdot C_3 + 5.254 \cdot 10^{-8} \cdot C_4$$

C_1, C_2, C_3 and C_4 are the activity concentrations from ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po. The equilibrium factor $F = C_{eRn}/C_{Rn}$ depends mainly on the indoor air exchange rate, the aerosol concentration in the room and the source surface to volume ratio of the room. Representative indoor F-values for low aerosol concentrations are 0.2 to 0.4 and for high aerosol concentrations 0.6 to 0.8.

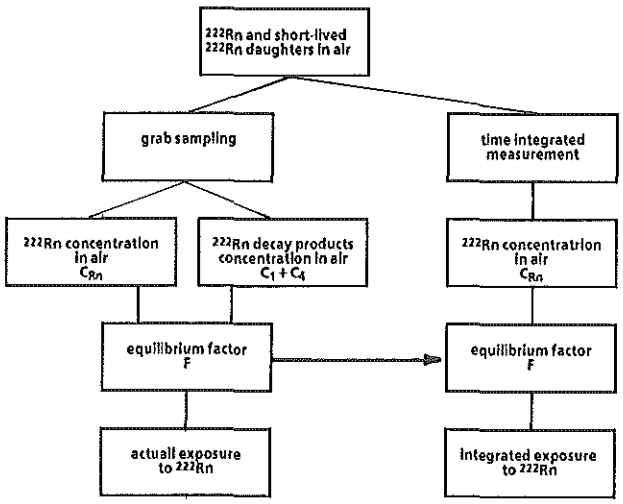

Fig. 3 Most frequently used techniques for the estimation of the radon exposure

Another aspect to be considered is the influence of unattached Rn daughters expected by the quantity f_p, which is defined as the ratio of the equilibrium-equivalent Rn concentration of the unattached activity Cf_{eRn} and that of the equlibrium-equivalent Rn concentration, $f_p = Cf_{eRn}/C_{eRn}$. In low ventilated rooms the mean value of the unattached fraction f_p of the equilibrium-equivalent Rn concentration was found to be 0.096 [1] - three times higher than previously proposed

by ICRP [17] - up to maximum values of 0.4 [2] and outdoor mean values of 0.02 [1]. Because of its smaller size and correspondingly greater diffusivity, a much larger dose contribution to the bronchial epithelium is expected from the unattached decay products than from those that are attached [3].

4 Measurement techniques

4.1 Active detector system

In general, active measurement techniques are applied for short-term, continuous and time integrated radon measurements using α-particle detectors, which require the relevant electronics, pumps and power supplies. For grab sampling of Rn gas these systems make use of ionisation chambers or scintillation chambers (Lucas cells), which count α-particles via scintillations from a ZnS/Ag layer using a photomultiplier. Filter methods analyse Rn decay products deposited on a filter. On the one hand, they make use of gross counting of α-, β- or γ-particles or α-spectrometry after aerosol particle deposition and, on the other hand, of a simultaneous spectrometry of the activity build-up already during the process of deposition. A representative slowing down spectrum of α-particles from ^{222}Rn in air is shown in Fig. 4 and design principles of detectors in Fig. 5.

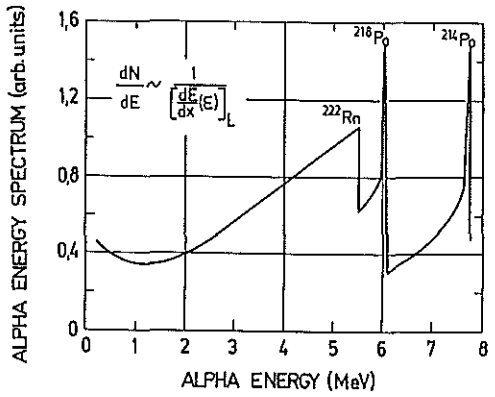

Fig.4 Slowing-down spectrum of alpha particles from ^{222}Rn in air

Retrospective in-vivo measurements of the Rn exposure of uranium miners, for instance, are based on the γ-measurement of ^{210}Pb in the skull (biological half-life 16 years) using a combination of three phoswich detectors. Within a KfK pilot study the lung exposure of uranium miners before 1955 have been recently measured with a lowest detectable level of 62 Bq corresponding to radon exposures of about 2.5 Sv (250 WLM) [4].

4.2 Passive detector systems

For the estimation of representative indoor Rn concentrations mainly two types of passive measurement techniques are applied, the adsorption of Rn in charcoal and diffusion chambers. Grab sampling measurements make use of active charcoal which absorbes radon within a short period of exposure (about three days).

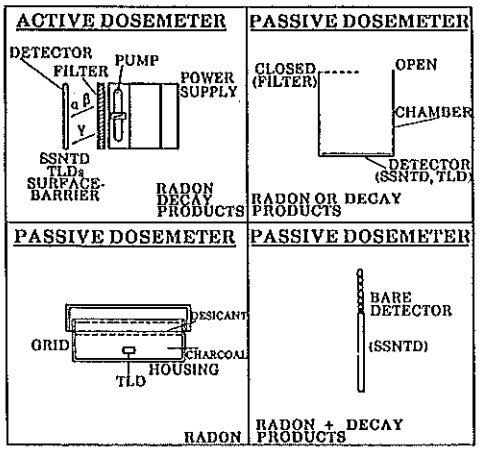

Fig.5 Design principles of radon dosemeters [8]

Afterwards the γ-rays from Rn decay products are counted in a NaI(Tl) detector device. The disadvantages of this technique are the strongly humidity dependence of the Rn absorption in charcoal and the deficiency in the memory effect. This technique does not integrate the radon concentration, and thus does not provide a mean value of the radon concentration.

Radon diffusion chambers are the most frequently applied passive detectors for a time integrated measurement of radon gas. They make use mainly of passive solid state nuclear track detectors (SSNTD) such as polycarbonate (Makrofol DE) and CR-39 inside a plastic box which is closed by a hydrophobic filter. After chemical etching of the plastic detector the counted track density of α-particles is a measure of the mean Rn concentration integrated over a long-term exposure period of about three month up to one year. Rn diffusion chambers have been applied for country-wide survey measurements of the Rn gas concentration. Instead of track etched detectors also thermoluminescent detectors and electret detectors have been used.

4.3 Estimation of the equilibrium factor

The knowledge of the equilibrium factor F of Rn and Rn daughters is of high importance for the calculation of the indoor radon exposure using Rn diffusion chamber results, but the measured F-values have been estimated up to now mainly with active α-spectrometers by measuring simultaniously both, the Rn daughters concentration ($C_1 + C_4$) in air and separatly the Rn gas concentration C_{Rn}. For indoor environments mean values between 0.3 and 0.4 have been adapted up to now, but the measured F-values vary between 0.1 and 0.6.

Another way to estimate $F = f(C_1 + C_4/C_{Rn})$ is the use of an open diffusion chamber or of a bare track etched detector for the simultanious measurement of Rn and Rn daughters ($C_1 + C_4 + C_{Rn}$) and the results of a closed diffusion chamber (C_{Rn}). These techniques show, however, a strong systematic uncertainty due to the need of a difference measurement $(C_1 + C_4) = (C_1 + C_4 + C_{Rn}) - C_{Rn}$.

A recently developed technique makes use of a Rn diffusion chamber and a bare track etched detector with a response in a small α-energy window resulting in a separate measurement of ^{214}Po [5,6]. The theoretical study of this technique which

estimates $F=f(C_4/C_{Rn})$ directly by two counts confirmes the experimental finding, that the measurement uncertainty of the difference method does not provide a sufficiently accurate estimation of F (Fig. 6) [6]. In the case, that the unattached fraction of Rn decay products varies from about 0.05 up to a value of 0.4, the relevant component of the systematic uncertainty for F=0.25, for instance, is expected to be +12 %/-36 % for the new technique (method II) compared to +112 %/-40 % for the difference method (method I), assuming counting errors of ±30 % and ±20 %, respectively. For the measurement of ^{214}Po, Makrofol DE has been recently optimized in the electrochemical etching (ECE) technique in order to offer a detector with an α-energy window between 6.1 and 7.5 MeV. This passive detector technique is a highly attractive alternative for active detector techniques due to the simultanious, time integrated measurement of both, the Rn concentration and the F-value of interest.

5 Indoor and outdoor radon concentrations

The most frequently used monitoring methods for country wide surveys are grab sampling or time integrated measurements of Rn gas or in the case of special studies α-spectrometry of short-lived Rn daughters in air [8]. Assumptions have to be made for a representative equilibrium factor F between Rn gas and Rn daughters using up to now short-term measurements.

Survey programmes for estimating the average Rn exposure of the public and its variation are mainly based on Rn diffusion chamber measurements which integrate the radon exposure over a period of at least several months. Integration over a long period of time seems to be the only way to avoid errors of the grab sampling technique. Representative results of radon surveys in various countries are given in Table 1.

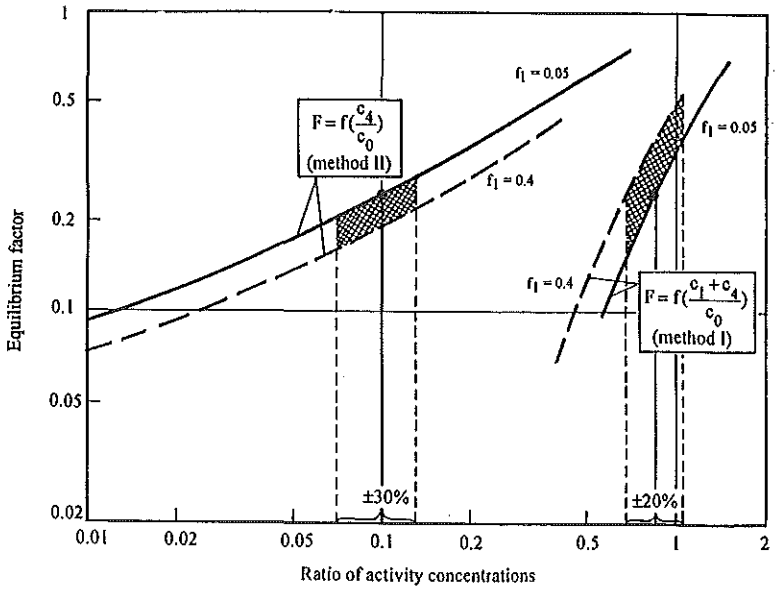

Fig.6 Estimation of the equilibrium factor as a function of activity concentration ratios using track etched detectors and time integrated measurements

Table 1: Mean indoor ^{222}Rn concentration in various countries [7-13]

Country	No of homes monitored	Rn concentration [1] [Bq/m3]	Median SD [%]	Reference
Austria	1000	15	9	Steinhäusler et al. 1982
Canada	9999	13	2.7	McGregor et al. 1980
Finland	4500	90	4	Castren et al. 1987
France	1552	50	2.6	Rannou 1987
Germany	5970	40	1.8	Urban et al. 1985
Ireland	1036	58	2	McLaughlin & Wasiolek 1988
Japan	251	19	2	Aoyama et al. 1987
Sweden	500	53 (69) [2]		Swedjemark & Mjones 1984
UK	2000	15	2.6	Green et al. 1985
USA	817	33	2.8	Nero et al. 1986
Switzerland	453	38	2.36	Völkle et al. 1992

[1] median value [2] apartements (detached)

Water content in the atmosphere, differences in the temperature and pressure between ground and the air are the main reasons for the strongly local and time dependent changes of the indoor and outdoor Rn concentration (Fig. 7). For the interpretation of a mean Rn concentration grap sampling results are not applicable because they do not average even the very large daily variation.

The outdoor Rn exposure depends on the Rn concentration of soil gas and the radon supply from the radium content in the ground. By diffusion into soil air and humidity, Rn reaches the atmosphere as well as the ground and surface water. Reasons for local variations in the outdoor Rn concentration near the ground are differences in the radium content of the soil, the porosity and the permeability of the ground. Table 2 gives representative radon concentrations for outdoors and inside buildings.

The resulting indoor radon concentration which exceeds the outdoor concentration depends on the radon emanation rate Q of the building materials, the size of the room and the exchange to the outdoor air. Equilibrium between indoor and outdoor air results in an indoor radon concentration

$$C_{Rn,indoor} = \frac{Q \cdot S}{\Phi \cdot V} + C_{Rn,outdoor}$$

with Q=exhalations rate, S=size of source surface, V=volume of the room, Φ= number of air exchanges (3 to 0.5/h for closed windows, for instance).

Table 2: Representative ^{222}Rn concentrations in the environment

^{222}Rn in the environment	
ground water	10-30 Bq·l^{-1}
surface water	<1-10 Bq·l^{-1}
soil air	1-10 kBq·m^{-3}
above ground	10 Bq·m^{-3}
indoor air	45 Bq·m^{-3}

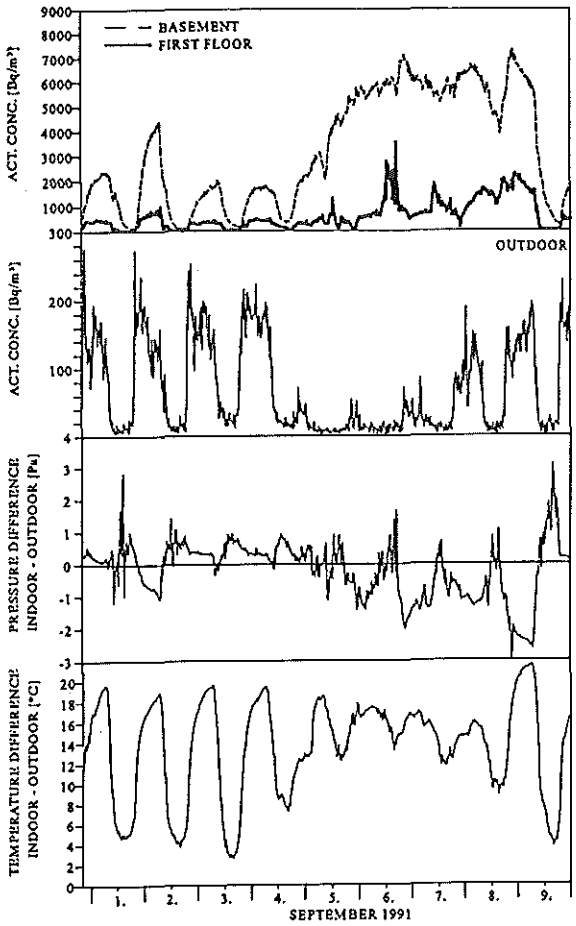

Fig.7 Time dependent variation of the indoor and outdoor Rn concentration and of pressure and temperature differences between indoor and outdoor [14]

6 Radon exposure

The estimation of the radon exposure caused by inhalation of Rn and its progeny in terms of the annual effective dose is not unproblematic because of the assumptions which have to be made for the dose conversion factors and the exposure conditions. According to ICRP 50 [17] and UNSCEAR [18] the dose conversion factor for an equilibrium-equivalent indoor ^{222}Rn concentration is 0.09 mSv (effective dose) per Bqm^{-3} and year. Representative data for the contributions of the indoor (19 h/d) and outdoor (5 h/d) exposure, and the Rn concentration with the relevant equilibrium factors (outdoor 10 $Bq \cdot m^{-3}$, F = 0.8, indoor 45 $Bq \cdot m^{-3}$, F = 0.35) result in Germany, for instance, in an effective dose of about 1.3 mSv. In 1 % of monitored dwellings the mean indoor Rn concentration exceeds a value of 220 $Bq \cdot m^{-3}$ [9].

In many countries, the individual and also the collective doses from radon in dwellings are substantially higher than those that would be permitted in occupational exposure. Action levels around 200 $Bq \cdot m^{-3}$ for Rn gas in dwellings are therefore introduced above which remedial actions are recommended, such as higher room ventilation or changes in the conventional building practice.

For higher levels of the Rn concentration at workplaces it seems to be necessary to consider an occupational radon exposure. This is, however, a controversly discussed problem up to now, because, on the one hand, the epidemiological evidence for a higher risk of lung cancer in those buildings is missing. On the other hand, there are general problems to monitore those workplaces. Under discussion are Rn gas concentrations of 400 up to 1000 $Bq \cdot m^{-3}$ taking into account a working time of 2000 h/year.

7 Radon risk

Generally, the risk of Rn related lung cancer is assessed by using information available from the uranium miners studies. With the present technique and uncertainty it is difficult if not impossible to distinguish the contribution of Rn only, smoking only or Rn with smoking to the number of lung cancers in the population. Effects on individuals exposed at lower concentrations, especially non smokers, are less certain and still controversly discussed. On the other hand, a significant correlation between high indoor Rn exposures in dwellings and the frequency of lung cancer has not been found up to now. It is therefore open for discussion wether the current ICRP concept [15-17] is applicable also for the public, which assumes a linear no-threshold relationsship between Rn exposure and the incidence of lung cancer and a quality factor for α-particles, which could be too high.

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SEASONAL VARIATION OF RADON CONCENTRATION IN EGYPTION DWELLINGS*

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ABSTRACT

Radon concentrations in Egyption dwellings were measured during winter and summer seasons. These measurements were done by using the KFK radon dosimeter which incorporate Makrofol track etch detector. Calibration of this detection system was done in the radon calibration facility of the Karlsruhe Nuclear Research Center, Germany.

The survey programme includes indoor and outdoor measurements in different towns in Egypt. The results of the field measurements have shown that indoor radon concentrations in Egypt varies between 3 and 47 Bqm with a mean value of 13 Bqm in the winter season and 7 Bqm in the summer season. The seasonal variation has shown an increase by a factor of 2 between winter and summer.

Comparisons between the measured data in Egypt and other reported data in different countrites are given.

1- INTRODUCTION:

The interest in radon measurements has increased during the last 10 years. One important reason for this is the increased knowledge of radon measuring techniques and the associated risks.

A number of passive and active techniques have been devloped by different laboratories for the monitorihg of radon and its decay products.

In this study, a summary is given about the application of nuclear track detectors for radon measurements in Egyptian dwellings (1), by using the KFK-passive radon dosimeter (2). This dosimeter consists of a polycarbonate nuclear track detector foil mounted inside a cup. The mouth of the cup is closed with a filter paper to allow radon to enter but to exclude decay products. After exposure, the detector foil is etched chemically and electrochemically and the tracks are counted by a microfisch reader.

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*This work has been done within the German Cooperation in Scientific Research & Technological Development KFA-IB with the Egyptian Atomic Energy Authority.

2- CALCULATION OF RADON CONCENTRATION:

The KFK-passive radon dosimeter was calibrated in the radon calibration facility of the Karlsruhe Nuclear Research Center, in Germany. In this facility, a dry radium-226 source is used to provide the measured quantities of radon-222 gas. A known concentration of radon can be circulated in a chamber of about 0.5 m volume, in wich the radon dosimeters can be irradiated. A constant flow rate is maintained during the whole exposure period. In the mean time, a surface barrier detector is located in the same place of the track etch detector in the radon dosimeter. The surface barrier detector is connected with a multichannel analyser for spectrometric measurements.

In this facility the radon concentration flow rate is directly correlated with nominal activity of the radium source. Also, the surface barrier spectrometer provides information about the energy distribution of alpha particles involved, and the relative contribution of each energy group. The radon concentration was calculated from the equation :

$$C = \frac{(N - N_o)\ 1000}{\epsilon \cdot t \cdot A}$$

Where
- c = Radon concentration in Bq m^{-3}
- N = Total tracks counted of the exposed foil
- N_o = Total tracks counted of the unexposed foil.
- A = Scanning area in cm^2
- t = Field exposure time in days (d).
- ϵ = Calibration factor in (Tracks. cm^3 / cm^2. KBq d.).

Based on intercomparison measurement (3). The calibration factor was found to be :

$$\epsilon = 15 \text{ Track. } cm^3 / cm^2 . \text{ KBq d.}$$

This factor is valid only for the KFK passive dosimeter by using Makrofol-DE 300 um thick to be etched under the previously mentioned conditions.

3- FIELD APPLICATION:

A survey program was made in dwellings situated largely in centers of population in Cairo, Alexandria, Damietta and Rosetta. The mentioned sites were supplied with one or two radon dosimeters placed in bedroom, or livingroom and outdoor in the balcony.

Measurements were made in two runs; one during the summer season and the other during the winter season for an exposure time of about 100 days each.

3.1 Indoor Measurements

After exposure, the detector foils were etched and evaluated. The lower limit of detection for these measurements was estimated empirically as 3 times the standard deviation of the unexposed background foils. The equivalent value of this limit in terms of radon concentration was found to be 3 Bq m . Table (1) shows summaries of indoor radon concentration in Bq m during winter and summer survey runs, respectively.

Table (1): A comparison of indoor radon concentration in Bqm during winter and summer seasons.

Season	Maximum	Minimum	Mean	Standard deviation	Coefficient of variation
Winter	47	3	14	11	83 %
Summer	13	3	7	4	49 %

As expected, the mean radon concentration during the winter season was found to be higher by a factor of two compared with that in summer season. This may attributed to the reduction in ventilation rates in dwelling during the winter time. Table (2) shows a comparison between indoor concentration during summer and winter season with other measurement carried out in Saudi Arabia (4) and Italy (5).

Table (2): Comparison of Indoor radon concentration (Bq m)
in different countries

Radon concentration Bq m	Egypt		Saudi Arabia		Italy	
	Summer	Winter	Summer	Winter	Summer	Winter
Maximum	13	47	85	160	122	158.1
Minimum	3	3	15	44	5.5	7.8
Mean	7	14	42	89	56.1	51.4
Standard D.	4	11	18	33	29.4	37.3
Coefficient of Variation	49%	83%	-	-	-	-
Reference	This work		(4)		(5)	

3.2 Outdoor Measurement.

Similarly, outdoor measurements were carried out in the same survey program. Table (3) shows summaries of the outdoor measurements during the summer and winter seasons.

Table (3): Outdoor radon concentration in Bqm^{-3} during
summer and winter seasons

Season	Maximum	Minimum	Mean	Standard deviation	Coefficien of variation
Summer	10	3	5	2	45%
Winter	23	3	11	5	46%

As expected, the higher mean level in winter (higher than in summer by a factor of two), results from the fact that the vertical dispersion is better in summer. This difference may be expected between day time and night measurements (6).

A comparison between the outdoor radon concentration in Bqm^{-3} mesured by different techniques in some countries is shown in Table (4). The differences in the mean values of radon concentration in this table, can be accomodated within the natural statistical fluctuations. It was also reported in the UNSCEAR report (1988) that, the annual average of population weighted outdoor radon concentration is 5 Bq m .

Table (4): Comparison of outdoor mean radon concentration in Bqm^{-3} in different countries and in Egypt

	Egypt Passive	UK Passive	Germany - spectroscopy	USA -	Slovenia, Yugoslavia Passive
Range in Bqm	5 - 11	3.4	6.7	8-12	5 - 20
Refernce	This work	7	7	7	8

Table (5) shows a comparison between indoor and outdoor mesurement in summer and winter seasons in Egypt. The difference between indoor and outdoor radon concentration was found to be relatively small due to the non-tight building style in Egyptian dwellings.

Table (5): A comparison between indoor and outdoor mean radon concentration

Season	Indoor Bqm^{-3}	Outdoor Bqm^{-3}	Difference Bqm^{-3}
Winter	14	11	3
Summer	7	5	2

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